THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R.

Volume XXIV, No. 8

August, 1954

(A Publication of the Academy of Sciences of the U.S.S.R.)

IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU

259 West 14th Street

New York 11, N.Y.

Printed in the United States

Annual subscription $95.00
Single issue 20.00

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HIGHER BARIUM PHOSPHIDES

S. A. Shchukarev, M. P. Morozova, and E. A. Prokofyeva

It was recently shown [1] that in the system barium-nitrogen, together with ordinary barium nitride Ba_3N_2, it is possible to obtain, in a state of thermodynamic equilibrium with their decomposition products, the higher nitrogen compounds. The existence of these higher barium nitrides could have been predicted on the basis of their heats of formation, determined with the aid of the isoatom method [2], for which reason their synthesis was undertaken.

With the aid of this isoatom method it is possible to show that in a series of analogous binary systems (systems, composed of a single element on the one hand, and of the elements of a single subgroup of the periodic system on the other hand) the forms of the thermodynamically stable compounds shift in the direction of enriching the components for which the atomization enthalpy* is lower. The higher barium nitrides are formed under conditions of high nitrogen pressure. Inasmuch as the atomization enthalpy of phosphorus (31.6 kcal) is considerably less than the atomization enthalpy of nitrogen (85 kcal), it may be assumed that the higher barium phosphides (BaP_2, BaP_3) can be obtained in a state of thermodynamic equilibrium at low pressures of phosphorus vapors.

Actually, it was found that the reaction of metallic barium with phosphorus vapors at a temperature of 400-450°, with subsequent removal of excess phosphorus by vacuum distillation at the same temperature, leads to the formation of a dark gray product having the composition BaP_3.

The chemical analysis method, carried out in the following manner, was used to establish the formula of this compound.

The substance was transferred to a tared ampoule in an atmosphere of dry carbon dioxide gas, after which the ampoule was sealed and weighed. The sealed ampoule containing the analyzed substance was placed in a vessel, from which the air was removed by evacuation. On reaching a vaccum of the order of 10^{-2} mm the evacuation was terminated, the ampoule was broken, and concentrated nitric acid was added dropwise and with extreme care to the vessel, the purpose of the nitric acid being to oxidize the phosphorus hydrides to orthophosphoric acid.

The subsequent determination of the amount of barium and of phosphcus was performed in the usual manner.

Found %:** Ba 59.95; P 39.90. BaP_3. Calculated %: Ba 59.65; P 40.35.

The heating of the compound having this composition in vacuum at a temperature of 740-840° leads to the partial removal of phosphorus and the formation of a product, the composition of which approximates BaP_2. Data on the composition of the preparations obtained in our experiments are given in the table.

TABLE

Ba (in %)	P (in %)	Atomic ratio
68.4	30.6	1 : 1.984
68.6	30.8	1 : 2.002
69.1	30.8	1 : 1.976
68.4	30.4	1 : 1.970

It should be mentioned that even extremely prolonged (up to 20 hours) heating of this preparation in vacuum at a temperature of 780-840° fails to lead to further removal of phosphorus and the formation of the ordinary phosphide having composition Ba_3P_2. As a result, it can be assumed that the decrease in the atomization enthalpy on going from nitrogen to phosphorus makes the form, Ba_3P_2, corresponding to the normal valencies of barium and phosphorus, thermodynamically unfavorable.

The X-ray pattern of the preparation having a composition corresponding to the formula BaP_2, contains all of the lines found in the X-ray pattern for BaP_3 and, in addition, contains a series of new lines. The preparations were obtained at different temperatures; consequently, despite the excellent agreement of the results of numerous analyses, it is still difficult for us to draw any final conclusions as to wherher BaP_3 is an individual substance.

The final decision as to the number of phases in the system barium-phosphorus can be made on the basis of tensimetric measurements. As yet, only the existence of the compound BaP_2 can be considered as being established.

* We designate as the atomization enthalpy the enthalpy of transforming the element from its standard state into the state of a single atomic pair, referred to one gram-atom.

** Average of 6 determinations.

In due time some consideration was given [3] to the phenomenon of secondary periodicity, a discovery made by Byron in 1915. It was also shown that the phenomenon of secondary periodicity is very clearly manifested in the enthalpy values for the formation of binary compounds from the elements of the major subgroups, especially in the case of those compounds in which the elements show a valency corresponding to the number of the group.

An increase in the enthalpy of formation is observed on transition from an element of the second series to one of the third, a decrease is observed when the transition is from the third to the fifth series, then an increase is observed when the transition is from the fifth to the seventh series, and, finally, a decrease is again observed on transition to the ninth series. Together with the secondary periodicity of the heats of formation, as is shown by our data, there also exists a secondary periodicity of the higher forms of thermodynamically stable compounds.

The higher thermodynamically stable compound of barium with nitrogen is BaN_2, with phosphorus it is apparently BaP_3. In any case, the stability of BaP_2, i.e., the compound that is analogous to the higher form of barium nitride (BaN_2), is considerably greater than the nitride.

As was shown in some preliminary experiments, the reaction of barium with arsenic failed to give any compounds that were very rich in the nonmetallic element.

SUMMARY

1. The esixtence of the compound BaP_2 in the system barium-phosphorus was established. Also, the existence of BaP_3 was not excluded.

2. In accord with the prediction, based on the isoatom method, it was experimentally established that there is an increase in bond strength when going from nitrogen to phosphorus.

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Received March 6, 1954.

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SOLUTION REACTIONS BETWEEN ZIRCONIUM NITRATE AND ALKALI METAL IODATES

II. THE COMPOSITION OF ZIRCONIUM IODATE PRECIPITATES WHEN ALLOWED TO STAND WITH SOLUTIONS CONTAINING POTASSIUM IODATE

M. I. Konarev and A. S. Solovkin

It was shown earlier [1] that hydroxyiodates are present in the precipitate that is obtained when potassium iodate is added to zirconium nitrate solutions. Precipitates having the two compositions given below were isolated:

1) $Zr(OH)_3IO_3 \cdot 4H_2O$ and 2) $ZrOH(IO_3)_3 \cdot 4H_2O$.

The monoiodate is precipitated from aqueous zirconium nitrate solutions with either small or large amounts of added potassium iodate. From nitric acid solutions zirconium monoiodate is precipitated only when small amounts of potassium iodate are added. When a large excess of potassium iodate is added to the solution the only product found in the precipitate is zirconium triiodate.

Both the monoiodate and the triiodate precipitates, being amorphous, on long standing with the mother liquors containing potassium iodate, are converted into fine crystals.

With the objective of establishing the relationship existing between the structure of the precipitate and its composition, we studied: 1) the change in the composition of the precipitates with time, and 2) the compositions of the crystalline precipitates.

EXPERIMENTAL

Crystallization rate of zirconium iodate precipitates. On allowing zirconium monoiodate to stand with the mother liquor, containing potassium iodate, the precipitate begins to crystallize but the process takes place very slowly. After allowing to stand for 1.5 months we are unable to obtain complete crystallization of the precipitates. When zirconium triiodate is allowed to stand with the mother liquors the crystallization of the precipitates proceeds much more rapidly, which process is favored by the presence of nitric acid in the solution, the function of the nitric acid being to prevent hydrolysis (Table 1).

The values given in Table 1 show that the reaction is not terminated with the formation of zirconium triiodate. On changing the structure of the precipitate the composition also undergoes a change. On standing with the mother liquor, the initially precipitated triiodate adds potassium and iodate groups, hydroxyl groups and water being removed from the compound (Experiment Nos. 3-6, 11, 12, 17 and 19).

The reaction of the triiodate precipitate with potassium iodate contained in the solution takes from several hours to many days, depending on the concentration of potassium iodate and the acidity of the solution. With increase in the solution concentration of potassium iodate, and also on lowering the acidity, the rate of change in composition increases, and the crystallization rate is accelerated. Only at extremely low acid concentrations (pH 2-3), due to hydrolysis of the precipitates (formation of $Zr(OH)_3IO_3 \cdot 4H_2O$) is their rate of reaction with potassium iodate markedly retarded.

The crystalline precipitates, in contrast to the amorphous precipitates, do not contain any water of crystallization. The compounds that are formed are less soluble than zirconium triiodate.

Composition of the crystalline zirconium iodate precipitates. The experiments were carried out with nitric acid and water solutions of zirconium nitrate. When working with nitric acid solutions the precipitant used was potassium iodate, dissolved in nitric acid, which also served to dissolve the zirconium nitrate. When working with water solutions of zirconium nitrate the precipitants used were mixtures of iodic acid with potassium iodate. In the starting nitrate solutions the amount of zirconium was about 1.4 g/liter. The precipitant was added in a volume equal to the volume of the zirconium nitrate solution.

TABLE 1

Change in the Composition of Zirconium Iodate with Time

Exp. No.	Time	Found in mother liquor (in g/ liter)		Found in precipitate (in %)						Ratio in the precipitate K : Zr : IO_3 : H_2O	Character of the precipitate
		IO_3	Zr	K	Zr	IO_3	NO_3	H_2O	Total		
					1.4 N HNO_3						
1	10 min.	15.9	11.0	None	12.59	73.16	0.04	9.91	95.7	0 : 1 : 3.03 : 4.0	Amorphous
2	3 hours	15.9	9.9	None	12.89	73.37	0.14	10.12	96.4	0 : 1 : 2.97 : 4.0	Amorphous
3	24 hours	15.5	9.6	6.14	8.82	84.67	0.02	2.90	96.7	1.62 : 1 : 5.01 : 1.6	Mixture of amorphous with crystalline
4	32 hours	15.1	7.0	6.70	6.55	87.01	–	0.15	99.5	2.39 : 1 : 6.93 : 0	Crystalline
5	72 hours	14.6	4.9	6.65	6.75	87.23	–	0.00	99.0	2.30 : 1 : 6.74 : 0	Crystalline
6	120 hours	14.7	5.1	6.64	6.77	87.32	–	0.04	99.2	2.29 : 1 : 6.73 : 0	Crystalline
					5.5 N HNO_3						
7	10 min.	32.2	15.8	None	12.52	75.12	0.12	10.10	97.7	0 : 1 : 3.13 : 4.1	Amorphous
8	8 hours	32.1	14.5	None	13.26	73.06	0.06	10.03	96.7	0 : 1 : 2.86 : 3.9	Amorphous
9	24 hours	32.2	14.5	None	13.13	72.53	–	9.71	95.3	0 : 1 : 2.88 : 3.8	Amorphous
10	33 hours	32.2	14.2		13.24	74.23	–	–	–	0 : 1 : 2.92	Amorphous
11	168 hours	31.2	10.0	5.43	8.10	84.22	–	–	97.8	1.56 : 1 : 5.42	Greater part crystalline
12	240 hours	30.9	6.4	6.16	7.44	85.70	–	–	99.3	1.93 : 1 : 6.00	Crystalline
					5.7 N HNO_3						
13	10 min.	69.2	13.3	None	11.85	74.80	0.04	–	–	0 : 1 : 3.29	Amorphous
14	1 hour	69.0	11.1	None	13.01	74.44	0.14	–	–	0 : 1 : 2.99	Amorphous
15	2 hours	68.7	10.4	0.7	13.00	74.49	–	–	–	0 : 1 : 2.99	Amorphous
16	5 hours	66.7	9.6	–	7.08	83.59	–	–	–	–	Crystalline
17	8 hours	66.4	7.4	6.24	7.14	85.40	–	–	–	2 04 : 1 : 6.24	Crystalline
18	12 hours	65.9	7.8	–	7.20	84.80	–	–	–	–	Crystalline
19	60 hours	65.5	5.9	6.03	7.13	85.11	–	–	–	1.97 : 1 : 6.23	Crystalline

In studying the variation in the composition of the precipitate as a function of the potassium iodate concentration and of the acidity of the solution, it was found necessary to make a large number of experiments. The obtained results are divided into two groups and are given in Tables 2 and 3.

The composition of each separately analyzed precipitate is not given in Table 2. In the table are given the potassium iodate concentration intervals, within which limits precipitates are obtained with varying amounts of iodate groups per 1 atom of zirconium. In Table 3 are given the results obtained on analyzing the precipitates with whole number ratios between the iodate groups and potassium.

The data given in Table 2 show that on increasing the concentration of potassium iodate, with the acidity of the solution kept constant, the amount of iodate groups and of potassium is increased with respect to the amount of zirconium found in the precipitate.

The formation of compounds with whole number relationships between the components is not characteristic for the crystalline zirconium iodates, for which reason sharp transitions in the compositions are not observed. Only by the method of judicious selection of the amount of excess potassium iodate (at the given acidity of the solution) is it possible to obtain precipitates with whole number relationships between the iodate groups and zirconium(6 : 1, 7 : 1, 8 : 1 and 9 : 1). At potassium iodate concentrations lower than that needed for the formation of the iodate with six iodate groups per 1 atom of zirconium, a portion of the precipitates remains amorphous.

The composition of the crystalline zirconium iodates is determined not only by the concentration of potassium iodate, but also by the acidity of the solution. With increase in the acidity the addition of iodate groups, and especially of potassium, is made difficult; consequently in order to obtain precipitates of the same composition in more highly aci-

dic solutions it is necessary to use a higher concentration of potassium iodate. When a mixture of iodic acid and potassium iodate is used as the precipitant, both the total concentration of iodate ions in solution and the ratio between iodic acid and potassium iodate possess considerable significance.

TABLE 2

Change in the Composition of Zirconium Iodate Precipitates with Change in the Acidity and Concentration of Potassium Iodate in the Solution

Concentration of acid in the solution	Amount of IO_3-groups in the precipitate per 1 atom of zirconium						Number of iodate groups found per 1 atom of potassium	Number of investigated precipitates
	from 6 to 7	from 7 to 8	from 8 to 9	from 6 to 7	from 7 to 8	from 8 to 9		
	IO_3 concentration in the solution (in moles/liter)			Number of K atoms found per 1 atom of zirconium				
Nitric acid solutions								
0.18	0.070-0.095	0.095-0.150	Not formed on saturating the solution with KIO_3	2.0-2.3	2.3-2.6	–	~ 3	9
0.48	0.080-0.120	0.120-0.240						15
0.98	0.085-0.130	0.130-0.270						16
1.75	0.100-0.140	0.140-0.310						14
3.3	0.135-0.190	0.190-0.300	0.300-0.400*	1.6-2.0	2.0-2.6	2.6-2.8	~ 3	12
4.2	0.150-0.250	0.250-0.320	Not formed					8
Iodic acid solutions								
0.062	Not determined	0.140-0.310	0.310-0.358	2.0-2.35	2.35-2.65	3	~ 3	5
0.084	0.100-0.140	0.140-0.290	0.290-0.350					13
0.166	Not determined	0.275	0.235-0.284					3
0.248	0.270	0.378-0.390	0.280-0.305					10

TABLE 3

Composition of the Precipitates with Integer Amounts of Iodate Groups

Number of iodate groups found per 1 atom of zirconium in the precipitate	Amount in the precipitate (in %)				Ratio in the precipitate		Number of investigated precipitates
	K	Zr	IO_3	Total	K : Zr	IO_3 : K	
3	None	12.92	75.17	88.09	–	–	8
6	6.40	7.33	85 35	99.1	2.04	3.00	6
7	6.19	6.36	86.41	99.0	2.25	3.16	4
8	6.24	5.69	87.45	99.4	2.60	3.09	8
9	6.49	5.18	88.95	100.6	2.93	3.06	3

In the experiments with the nitric acid solutions we were able to obtain precipitates containing only up to 8.6 iodate groups per 1 atom of zirconium. In the experiments where mixtures of iodic acid and potassium iodate served as the precipitants, we were able to obtain precipitates containing up to 9 iodate groups per 1 atom of zirconium.

Two atoms of potassium are present in the precipitate containing 6 iodate groups per 1 atom of zirconium. Further increase in the number is more rapid for the iodate groups than it is for potassium. The following rule holds true for expressing the relationship that exists between increase in the number of iodate groups and the increase in potassium: in all crystalline precipitates, in which number are also included those precipitates having fractional ratios between the iodate groups and zirconium, the ratio of the iodate groups to potassium is expressed by a constant, equal to 3.

* The mole ratio of IO_3 to zirconium was 8.6 : 1.

The constancy of the ratio values between the iodate groups and potassium (with fractional ratios between the iodate groups and zirconium, also between potassium and zirconium) is possible only if the conditions are such that the mixtures of compounds that are formed possess a 3:1 ratio of iodate groups to potassium. Such compounds can be characterized by the ratios $K:Zr:IO_3 = 1:1:3$, 2:1:6, 3:1:9, 4:1:12, etc.

It is possible to make the proper selection on the basis of the results presented in Table 3.

The data given in this table show that the first variant (with the ratio $K:Zr:IO_3 = 1:1:3$) is excluded, inasmuch as the precipitates containing 3 iodate groups for 1 atom of zirconium do not contain any potassium. Compounds containing 12 and more iodate groups for 1 atom of zirconium should be excluded, inasmuch as not one of the obtained precipitates contained more than 9 iodate groups and more than 3 atoms of potassium for 1 atom of zirconium (even at maximum saturation of the solution with potassium iodate).

In the precipitates containing 7 and 8 iodate groups for 1 atom of zirconium the ratios between potassium and zirconium are expressed by fractional values; consequently these precipitates can be considered as being mixtures.

An examination of the numerical analysis results leads to the conclusion that on long standing the triiodate is converted only into two compounds, the hexaiodate and the enaiodate. The first compound contains 2 atoms of potassium, while the second compound contains 3 atoms of potassium (Table 3).

Zirconium hexaiodate and enaiodate can be depicted as being either binary salts or as being complex compounds.

Observations show that both compounds are readily hydrolyzed by water with transformation into hydroxy compounds. When dissolved in nitric acid the hexaiodate and enaiodate decompose into simple ions, consequently the subsequent addition of sufficient potassium iodate to the nitric acid solution results in the separation of the triiodate in the precipitate.

Taking into consideration the properties of the precipitates, it seems expedient to depict them as being binary salts – $Zr(IO_3)_4 \cdot 2KIO_3$ (hexaiodate) and $Zr(IO_3)_4 \cdot 3KIO_3 \cdot 2HIO_3$ (enaiodate).

SUMMARY

1. Freshly precipitated zirconium iodate is not stable. On long standing with the mother liquor the precipitate reacts with potassium iodate and iodic acid to yield the hexaiodate and the enaidoate.

2. In the formation of the hexaiodate and enaiodate the precipitates are transformed from the amorphous state to the crystalline state. The rate of transformation to the crystalline state is accelerated with increase in the concentration of potassium iodate in the solution (for nitric acid solutions) or with increase in the concentration of iodic acid and potassium iodate (in the precipitation of zirconium from water solutions of the nitrate).

3. The hexaiodate, devoid of any enaiodate as impurity, is formed only in very narrow concentration limits of potassium iodate in the solution (the limits change with change in the acidity).

The enaiodate is formed at high concentrations of iodate ions in the solution and at favorable relative concentrations of iodic acid and potassium iodate.

Mixtures of the hexaiodate and enaiodate are most frequently found in the precipitates, the relative amounts of which change with change in the concentrations of iodate ions and potassium in the solution.

4. Independent of the average composition of the mixtures, the amount of iodate groups in them with respect to potassium is expressed by a constant value, equal to 3, which value is conditioned by the composition of the hexaiodate and enaiodate present in the mixture.

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Received March 15, 1954

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NIOBATES AND TANTALATES OF ALKALI EARTH METALS

I. Metaniobates and Metatantalates of Calcium, Strontium and Barium

V. A. Pchelkin, A. F. Efimov and A. V. Lapitsky

The first information on the preparation of anhydrous metaniobates of the alkali earth elements was published in 1875 [1]. The anhydrous metatantalates of the alkali earth metals were synthesized at a considerably later date [2,5]. The authors of the indicated papers make no mention of studying the properties of the given compounds.

We set ourselves the task of synthesizing the metaniobates and metatantalates of the alkali earth metals, and also of studying some of their properties.

EXPERIMENTAL

Starting materials. The pentoxides of niobium and tantalum were obtained by the method of separating the technical mixture. Chemically pure gades of calcium, strontium and barium carbonates were used.

Preparation of the metaniobates and metatantalates of the alkali earth metals. The metaniobates and metatantalates of calcium, strontium and barium were obtained by fusion of equimolecular amounts of niobium (or tantalum) pentoxide and the corresponding carbonate of the alkaline earth metal. In order to accelerate the fusion, potassium fluoride was used as flux, added in an amount equal to 0.1 weight part on the weight of the mixture. The finely pulverized mixtures were poured into crucibles, which were then heated in the furnace for a period of 3 hours at 1200°. A white crystalline substance was obtained after fusion.

In order to remove potassium fuloride the substance was pulverized and treated with water. After drying at 120° the salt was analyzed for the amount of niobium (or tantalum) pentoxide and metal oxide. Weighed samples of the salts were fused with an excess of ammonium hydrosulfate in porcelain crucibles. After complete cooling, the formed transparent melts were leached with a solution of ammonium oxalate. The insoluble deposits contained the sulfates of the alkaline earth metals.

After removal of the sulfates, the oxalate solutions were heated on the water bath and treated with a freshly prepared 2% tannin solution. The niobates were precipitated from weakly alkaline solution, while the tantalates were precipitated from weakly acidic solution. The analysis results obtained for the salts are given below.

Analysis of calcium metaniobate

Weight of substance 0.2566 and 0.1470 g

Found %: Nb_2O_5 81.98, 82.00; CaO 17.26, 17.20. $Ca(NbO_3)_2$. Calculated %: Nb_2O_5 82.61; CaO 17.39.

Analysis of strontium metaniobate

Weight of substance 0.2462 and 0.2256 g

Found %: Nb_2O_5 71.96, 71.58; SrO 27.54, 27.38. $Sr(NbO_3)_2$. Calculated %: Nb_2O_5 72.33; SrO 27.67.

Analysis of barium metaniobate

Weight of substance 0.1826 and 0.1830 g

Found %: Nb_2O_5 63.20, 63.21; BaO 36.34, 36.30. $Ba(NbO_3)_2$. Calculated %: Nb_2O_5 63.49; BaO 36.51.

Analysis of calcium metatantalate

Weight of substance 0.3044 and 0.3144 g

Found %: Ta_2O_5 88.69, 88.53; CaO 11.65, 11.42. $Ca(TaO_3)_2$. Calculated %: Ta_2O_5 88.75; CaO 11.25.

Analysis of strontium metatantalate

Weight of substance 0.2866 and 0.1516 g

Found %: Ta_2O_5 80.18, 81.13; SrO 19.88, 19.78. $Sr(TaO_3)_2$. Calculated %: Ta_2O_5 80.97; SrO 19.03.

Analysis of barium metatantalate

Weight of substance 0.1614, 0.2218 g

Found %: Ta_2O_5 74.66, 74.39; BaO 25.59, 26.08. $Ba(TaO_3)_2$. Calculated %: Ta_2O_5 74.29; BaO 25.71.

The chemical analysis results show that we had obtained the anhydrous metaniobates and metatantalates of the alkaline earth metals, of which the majority had been obtained for the first time.

In order to be sure that the reaction had gone to completion in the heating of mixtures of niobium (or tantalum) pentoxide with the carbonates of the alkaline earth metals, we made X-ray phase analyses of the mixtures, which in all cases showed the presence of a single phase.

Properties of the metaniobates and metatantalates of the alkaline earth metals. All of the investigated salts have high melting points. In the present study we conducted experiments to determine the volatility of all of the metaniobates and metatantalates of the alkaline earth metals.

The experimental procedure was described earlier. The volatility studies were made at atmospheric pressure and in vacuum. The duration of heating was 6 hours. The experimental results show that the investigated compounds possess thermal stability and are nonvolatile even in vacuum.

This property of the indicated salts can be understood when their properties are compared with the properties of the earlier described metaniobates and metatantalates of the alkali metals [3].

It should be mentioned that the metaniobates of calcium, strontium and barium change their color when heated in vacuum, acquiring a light gray cast. It has already been mentioned by us that a similar phenomenon is observed when the anhydrous metaniobates of the alkali metals are heated in vacuum.

As was indicated, the thermal stability and high melting points of these salts can be explained on the basis of the monolithic character of the ions NbO_3^{-1} and TaO_3^{-1} [4]. The properties of the metaniobates and metatantalates of calcium, strontium and barium can be considered in an analogous manner. Here also the monolithic metaniobate and metatantalate ions fail to exert a polarizing influence on the calcium, strontium and barium ions. Because of their nature, the latter ions fail to exert any appreciable polarizing action on the corresponding anion. This fact determines the character of the bond as being ionic, and conditions the high melting point and nonvolatility of the compounds. As was shown in the preliminary experiments, all of the metaniobates and metatantalates of the alkaline earth metals have a low solubility in water.

We studied the conductance of saturated solutions of all of the above indicated salts at 20°. The saturated solutions were prepared with double distilled water. The specific conductance was calculated with the aid of the formula $\chi = KW$, where K is the vessel constant, $W = \frac{1}{R_{soln.}}$.* The measurement results are given in the table.

TABLE

Specific Conductance of Saturated Solutions of Anhydrous Metaniobates and Metatantalates of Calcium, Strontium and Barium at 20°. (Vessel Constant 0.4433)

Salt	Specific conductance ($ohm^{-1}\ cm^{-1}$)
$Ca(NbO_3)_2$	$1.22 \cdot 10^{-5}$
$Sr(NbO_3)_2$	$2.06 \cdot 10^{-6}$
$Ba(NbO_3)_2$	$3.81 \cdot 10^{-6}$
$Ca(TaO_3)_2$	$2.14 \cdot 10^{-5}$
$Sr(TaO_3)_2$	$0.99 \cdot 10^{-5}$
$Ba(TaO_3)_2$	$1.42 \cdot 10^{-5}$

Attention is directed to the fact that barium metaniovate and barium metatantalate possess a greater solubility than do the corresponding strontium salts, the latter possessing an extremely low solubility. On the other hand, it is a striking fact that the metatantalates show a greater solubility than do the metaniobates. The absence of literature data on the mobility of the ions NbO_3^{-1} and TaO_3^{-1} makes it impossible to calculate the solubility values for the investigated salts from the specific conductance data.

SUMMARY

1. The anhydrous metaniobates of strontium and barium and the metatantalates of calcium, strontium and barium have been synthesized.

2. It was established that all of the indicated salts and calcium metaniobate are thermally stable and do not possess any noticeable volatility even in a vacuum.

* The specific conductance of water was $1.4 \cdot 10^{-6}\ ohm^{-1}\ cm^{-1}$.

3. The specific conductance of saturated solutions of the anhydrous metaniobates and metatantalates of the alkaline earth metals was measured at 20°.

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Received January 3, 1954.

Moscow State University

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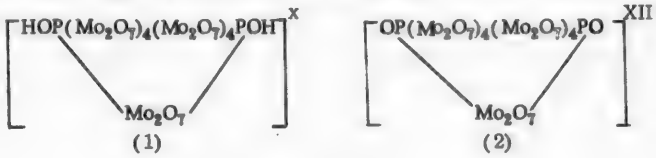
STRUCTURE OF PHOSPHO-9-MOLYBDIC (LUTEOPHOSPHOMOLYBCID) ACID

E. A. Nikitina and O. N. Sokolova

The question of the basicity and structure of the inner sphere of unsaturated heteropoly acids with the ratio $RO_x : NeO_y = 1 : 9$ is completely obscure; there are indications in the literature that these acids are six ten and twelve basic [1]. In 1953 Dawson [2], using X-ray structure analysis and electronographic methods, made an attempt to determine the structure of potassium luteophosphotung state, however, the carefully executed work made it possible to establish only the position of the tungsten atoms in thes salt; as regards the distribution of the oxygen atoms and in part of phosphorus, for the solution of this problem Dawson depended to a considerable degree on the earlier work of Keggin [3]; Dawson was simply unable to determine the position of the potassium ions and the water molecules. It should be mentioned that an analysis of the compound used in the investigation is not given in Dawson's paper, and the unverified gross formula assigned to it is $3K_2O \cdot P_2O_5 \cdot 18WO_3 \cdot 14H_2O$.

One of the positive results of the investigation is Dawson's conclusion that the heteropoly acids of the 9th series are binuclear complexes. As a result, using X-ray structure analysis and electronographic methods, Dawson confirmed that general configuration of complex molecules that is also assigned to them from coordination studies. However, all of the former problems relating to the structure of heteropoly acids of the 9th series, like the matter of their basicity, the structure of the inner sphere, the character of the addenda, etc., remained unsolved.

A method was developed by us for the preparation of luterophosphomolybdic acid [4]; the possibility of having any desired amount of this compound at our disposal permitted us to study the question of its structure. The syntheses of the sodium, potassium and ammonium salts show that the compound is hexabasic, the synthesis of the guanidine salt indicates that it is dodecabasic; the determination of the equivalent conductance when luteophosphomolybdic acid is neutralized with sodium hydroxide indicates that it is octabasic. As a result, the question of the basicity of luteophosphomolybdic acid remains debatable. For its soltuion and in order to elucicate the structure of the inner sphere the only idea that could serve as a guide in our investigation was the coordination study. In accord with this theory two structural formulas are possible for luteophosphomolybdic acid; in accord with the first formula the heteropoly acid is decabasic and functions as a hydroxy compound; the second formula depicts it as being a dodecabasic oxo acid; in both cases the inner sphere of the compound is thought to be a binuclear complex.



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EXPERIMENTAL

Our experiments on the potentiometric titration of luterophosphomolybdic (subsequently we will write it as lpm) acid solutions with solid sodium hydroxide were conducted in the presence of a quinhydrone electrode. During the titration process the latter dissolved; the minimum conductance was not attained even on adding 40 equivalents of alkali. In subsequent work we obtained soluble sodium salts of lpm acid by the method of gradual replacement of all of the possible hydrogen ions in the acid molecule, and investigated the obtained compounds.

We were able to establish that lpm acid is a strong acid: the pH of a 0.01 M solution, determined by the colorimetric method, is 0.5.

As is known, the heteropoly acids are decomposed by alkalies, as a result of which the danger exists that the direct action of alkali on lpm acid will cause the decomposition of the latter. Actually, when the calculated amount of alkali is rapidly added in one dose the solution warms up considerably and a cloudiness appears due to the precipitation of molybdic acid. A sample of the solution showed the presence of saturated phosphomolygdic acid, i.e., partial decomposition had taken place. When the alkali is added slowly by equivalents but without cooling, it was noted that partial transformation of lpm acid into saturated phosphomolybdic acid had taken place.

As a result of the performed orientating experiments it was found that it is possible to avoid the decomposition of

the heteropolyanion if 10 N sodium hydroxide solution is slowly (dropwise) added to a 40-45 % solution of lpm acid at a temperature not exceeding 30°.

The synthesis of the sodium salts was carried out in the following manner: the solution of lpm acid was prepared and analyzed for the total amount of the oxides P_2O_5 + MoO_3; then to a known weight of such a solution the calculated amount of standard sodium hydroxide solution was slowly added in portions with good mixing, each portion being equal to one equivalent; successive portions were added at 2-3 minute intervals. During neutralization the solution was cooled with a mixture of ice and water, and its temperature was maintained at 20-30°. Under these conditions no evidence of decomposition was observed.

The isolation of crystalline salts from the obtained solutions was associated with great difficulties. When concentration of the clear orange-yellowish solutions was attempted by boiling or by evaporation on the water bath at 65-70° it was established that the complex undergoes decomposition in both cases. It was noticed that the stability of the salt solutions increases in accord with increase in the number of equivalents of alkali added, but not in a single case was it possible to use the inidcated concentration methods without incurring some decomposition. Some experiments were performed on evaporation of the salt solutions in vacuum (water suction pump) at a temperature of 65-70°. At first the evaporation proceeded satisfactorily, but with increase in the concentration of the solution it was noticed that sirupy solutions began to form, these solutions later congealing into dense vitreous masses. We finally had to settle on the isothermal evaporation ot the salt solutions in desiccators over sulfuric acid at 18-20°. But even in the given instance the isolation of individual crystalline compounds proved to be an extremely rare occurrence. For the investigations it was found necessary to isolate the crystallline compounds in the presence of mother liquor.

In subsequent work the water medium was replaced by alcohol. It was established that lpm acid is readily soluble in alcohol; a 40-45 % alcohol solution of the acid is stable for long periods of time (about a month), provided there are no significant variations in the storage temperature.

The monosubstituted sodium salt of lpm acid was prepared in alcohol solutions in a manner analogous to its synthesis in water medium; the obtained salt solution was more stable than the corresponding water soltuion.

Next the problem reduced itself to evaporation of the alcohol without incurrring decomposition of the salt. Attempts to use the water bath for this purpose failed to give positive results. Attempts were made to evaporate the alcohol solutions at room tempeature; for this purpose the salt solutions were poured in large watch glasses and allowed to stand on the bench. The disadvantages of this method were the vigorous reduction of hexavalent molybdenum by the heteropoly anion; consequently, we finally decided to use the method of isolating the salt crystals form aqueous solutions.

A 40-45% solution of lpm acid was prepared and to it was added, dropwise and with constant sitrring, the calculated amount of standard sodium hydroxide solution in portions corresponding to one equivalent on the amount of acid taken; the intervals between individual alkali additions were kept at 5-6 minutes and, as was indicated above, the solutions were cooled. The obtained clear orange salt solutions were cyrstallized under isothermal conditions.

In order to avoid reduction of the molybdenum under the influence of light and sharp temperature changes, the desiccators were kept in a dark cool place, the temperature of which changed but slightly up to the separation of a sufficient amount of crystals, inasmuch as on attaining a certain degree of concentration a slight movement of the vessel or stirring of the solution toward the end of evaporation was sufficient to cause complete solidification (super saturation).

As the result of prolonged and exact operation with this method we wereable to isolate all of the sodium salts of lpm acid, ranging from the mono- to the dodecasubstituted compound.

The analysis results for the obtained sodium salts of lpm acid are given in Table 1, as well as the pH measurements of the mono-, hexa- and dodecasubstituted salt solutions, determined by the colorimetric method.

To determine the amount of water about 1 g of the salt was dried at 100-110° for 1hour, then heated up to 300°, maintained at this temperature for about 1.5 hours and then carefully ignited in the burner flame for 2-3 minutes. The loss in weight corresponded to the water content.

P_2O_5 and Na_2O were determined in the salts by the earlier described method [6]. MoO_3 was determined by difference.

When alakli was added in an amount equal to 13 equivalents per mole of acid the color of the latter solution changed from orange to pale green; in accord with increase in the degree of evaporation in the desiccator the color became somewhat more intense but it retained a greenish cast even after the addition of hydrogen peroxide. After stand-

ing for a short time white crystals began to appear on the surface of the solution, and soon after this the solution was transformed into a dense mass of ill-defined crystals. When the mass was filtered on a Nutsch filter a yellowish-green filtrate was obtained, while the precipitate was a mixture of white and pale green clumps, the separation of which did not appear possible.

The obtained compound was analysed for the amount of H_2O, P_2O_5 and Na_2O. The analysis results are given in Table 2.

TABLE 1

Analysis Results for the Sodium Salts of Lpm Acid

Degree of substitution in the salt	Found H_2O (in %)	Found based on anhydrous composition (in %)			Calculated from the formula (in %)			pH of the solution (0.01 M)
		Na_2O	P_2O_5	MoO_3	Na_2O	P_2O_5	MoO_3	
Monosubstituted	9.71	1.21	5.13	93.66	1.12	5.14	93.74	~ 1
	10.22	1.17	5.15	93.68				
Disubstituted	10.13	2.33	5.06	92.61	2.22	5.08	92.70	–
	17.38	2.29	5.08	92.63				
Trisubstituted	9.67	3.20	5.05	91.75	3.29	5.02	91.63	–
	16.27	3.39	5.00	91.61				
Quadrisubstituted	17.73	4.29	4.96	90.75	4.34	4.97	90.69	–
	16.67	4.40	4.91	90.69				
Pentasubstituted	11.12	5.42	4.90	89.68	5.37	4.92	89.71	–
	10.79	5.31	4.83	89.86				
Hexasubstituted	9.82	6.23	4.83	88.94	6.37	4.86	88.77	~ 4.5
	11.30	6.35	4.84	88.81				
Heptasubstituted	18.03	7.24	4.81	87.95	7.35	4.81	87.84	–
	10.41	7.61	4.90	87.49				
Octasubstituted	16.84	8.26	4.70	87.04	8.32	4.76	86.92	–
	16.28	8.31	4.72	86.97				
Nonasubstituted	12.20	9.37	4.75	85.88	9.26	4.71	86.03	–
	17.78	9.50	4.77	85.73				
Decasubstituted	10.54	9.95	4.68	85.37	10.19	4.67	85.14	–
	11.42	10.35	4.60	85.05				
Undecasubstituted	11.47	11.23	4.66	84.11	11.09	4.62	84.29	–
	11.79	11.31	4.67	84.02				
Dodecasubstituted	16.48	11.80	4.53	8.67	11.98	4.57	83.45	~ 6.5
	17.55	11.91	4.50	8.59				

TABLE 2

Analysis of the Compound Obtained on Adding 13 Equivalents of Alkali to 1 Mole of Lpm Acid

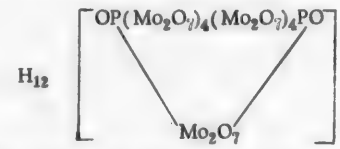
Compound	Found (in %)	Found based on anhydrous composition (in %)	Calculated from the formula (in %)	
			$3Na_2O \cdot P_2O_5 \cdot 14MoO_3$	$2Na_2O \cdot P_2O_5 \cdot 14MoO_3$
H_2O	11.63	–	–	–
P_2O_5	5.38	6.09	6.06	5.43
Na_2O	5.92	6.70	7.96	6.22
MoO_3	–	87.21	85.98	88.35

According to the given analysis, the obtained crystals are the trisubstituted salt of phospho-7-molybdic acid with the disubstituted salt of the same series being present as impurity.

Apparently, the addition of one equivalent of alkali to a solution of dodecasubstituted sodium luteophosphomolybdate leads to the decomposition of the latter with the formation of unsaturated heteropolyaacid salts less rich in molybdenum.

The fact that we were able to prepare highly substituted and readily soluble sodiums salts of lpm acid confirmed the validity of the coordination theory, which theory admits the multibasicity of heteropoly acids also with respect to unsaturated compounds, in which number lpm acid is included.

On the basis of the performed synthesis the structure of the hydroxy compound should be rejected and it should be assumed that lpm acid, being dodecabasic, is an oxo compound, having a structure corresponding to the formula



As a result, it was established that luteo acids with phosphorus as the complexing agent, as was to be expected from the coordination theory, are dodecabasic and not hexabasic, as many foreign investigators had thought up to the present time.

Viscosimetric study of sodium salt solutions of lpm acid. We studied the densities and viscosities of different concentrations of the mono-, hexa- and dodecasubstituted sodium salt solutions of lpm acid at 20°.

The analysis results for the salts used in the investigation are given in Table 3.

TABLE 3

Analysis Results for Sodium Luteophosphomolybdate

Salt composition	Found, based on anhydrous composition (in %)			Calculated from the formula (in %)		
	Na_2O	P_2O_5	MoO_3	Na_2O	P_2O_5	MoO_3
Monosubstituted	1.17	5.15	93.68	1.12	5.14	93.74
Hexasubstituted	6.23	4.83	88.94	6.37	4.86	88.77
Dodecasubstituted	11.80	4.53	83.67	11.98	4.57	83.45

The investigations were carried out in a glass thermostat equipped with a stirrer. Glass pycnometers, having approximate volumes of 1.3 and 0.25 ml, were used for the specific gravity determinations. Ostwald viscosimeters were used to study the viscosities of the solutions.

The viscosity was calculated from the formula $\eta = \eta_0 \frac{dt}{d_0 t_0}$, where η_0 is the viscosity of water at the investigated temperature in poises, d and t are the specific gravity and rate of flow for the investigated solution, while d_0, t_0 are the same values for water (Table 4, Figures 1 and 2).

For orientation purposes in connection with the preparation of solutions for studying the viscosities of the salts, we determined the solubility of the mono-, hexa- and dodecasubstituted salts in water at 20°.

The solubilities of the salts were based on the anhydrous compound (in %): for the monosubstituted salt 68.81, for the hexasubstituted 67.26, and for the dodecasubstituted 68.25.

From the presented graphs it can be seen that the viscosity isotherms appear as smooth lines. The absolute viscosity values for the salt solutions are less than for the free acid; the solubility values also differ from the solutility of the acid and differ between themselves; the pH values of the salt solutions are different. This permits drawing the conclusion that all of the obtained sodium salts of lpm acid are individual chemical compounds.

The viscosity and specific gravity values for the mon-, hexa-, and dodecasubstituted salts are extremely close. This proximity in the properties of salts with different degrees of substitution permits considering the heteropoly compounds in some cases exhibit the properties of compounds of the daltonide type, while in other properties their berthollide nature is more clearly defined.

In the work [5] it was established that heteropoly acids are two-layered complexes. The complexing agent coordinates 6 nonequivalent oxygen ions, which in their turn are surrounded in lpm acids by MoO_3 radicals. Apparently, the MoO_3 radicals are connected between themselves by a common oxygen bond, as a result of which Mo_2O_7 radicals are formed. These oxygen bonds in the case of molybdenum are more stable than they are in the case where they are found in the inner sphere of WO_3 radicals. Actually, during the gradual addition of KOH to silicotungstates the WO_3

groups were removed one at a time from the inner sphere; in the case of adding one equivalent of NaOH to the dodecasubstituted sodium luteophosphomolybdate we obtained the cleavage of two MoO_3 groups.

TABLE 4

Specific Gravity and Viscosity of Sodium Luteophosphomolybdate Solutions

Salt Composition	Solution concentration (in %)		d	$\eta \cdot 10^2$
	Weight	Molal		
Monosubstituted	24.92	0.2157	1.25	1.42
	37.47	0.3887	1.42	1.87
	51.31	0.6790	1.68	3.10
	61.19	1.0164	1.94	6.48
	66.88	1.2981	2.13	10.43
Hexasubstituted	27.61	0.2346	1.28	1.51
	37.21	0.3642	1.41	2.06
	52.64	0.6807	1.70	3.41
	60.38	0.9310	1.90	5.70
	63.33	1.0537	1.98	5.87
Dodecasubstituted	25.51	0.1981	1.25	1.33
	37.72	0.3499	1.45	1.92
	44.37	0.4602	1.56	2.32
	59.02	0.8280	1.88	5.81
	64.39	1.0374	2.01	8.27

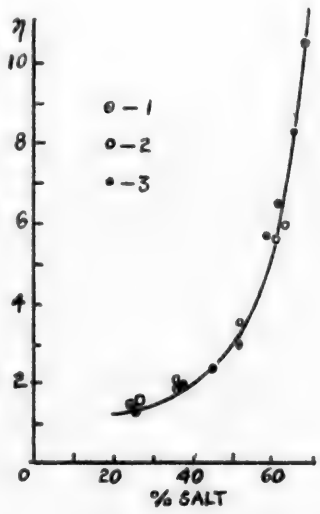


Fig. 1. Curve for the relationship between viscosity and salt concentration in the solution.

1 - Monosubstituted, 2 - Hexasubstituted, 3 - Dodecasubstituted

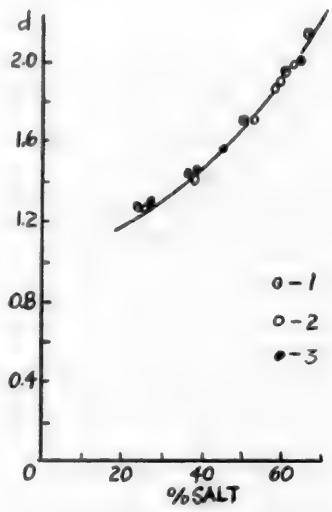


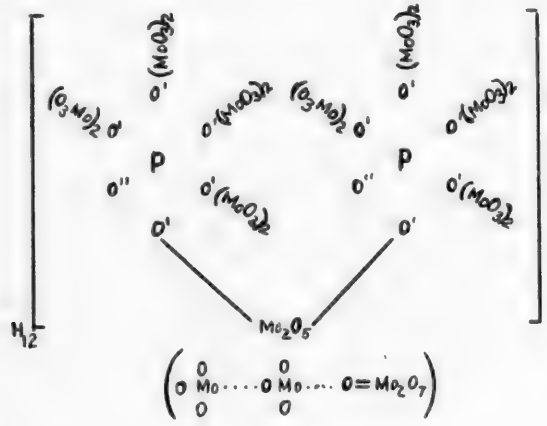
Fig. 2. Curve for the relationship between specific gravity and salt concentration in the solution.

1 - Monosubstituted, 2 - Hexasubstituted, 3 - Dodecasubstituted

The first manifestation of difference in behavior for the coordinated groups WO_3 and MoO_3 should be attributed to the structure of the tungsten and molybdenum ions themselves. Apparently, the inner sphere radicals MoO_3 or

WO_3 are arranged in the inner sphere of heteropoly acids in a manner similar to the arrangement of the oxygen atoms in potassium dichromate. This fact makes it possible to give the structural formula for lpm acids. According to Pfeiffer we retain the nonequivalent oxygen atoms in this formula.

Under the influence of alkali the bond between the oxygen and two MoO_3 groups is broken; either the MoO_3 groups are removed by single cleavage from the number surrounding both central ions or the bridge is destroyed, it is impossible to definitely say which is true inasmuch as it is necessary to study the propetries of the phospho-7-molybdates in order to find the answer.



Two oxygen ions, surrounding the central ion, create the bridge bond; apparently, because of such a bond character the luteo acid is considerably less stable than the saturated acid.

SUMMARY

1. The 12 sodium salts of lpm acid were obtained for the first time.

2. Lpm acid is a dodecabasic acid, possessing the structure of an oxo compound.

3. Water solutions of all of the obtained sodium salts show an acid reaction.

4. The addition of the thirteenth equivalent of NaOH to a solution of lpm acid resulted in the separation of the trisubstituted salt of phospho-7-molybdic acid with the disbustituted salt being present as impurity, under these conditions the lpm acid undergoes decomposition with the formation of compounds that are less rich in molybdenum.

5. All of the obtained sodium salts of lpm acid are readily soluble in water and in alcohol.

6. The viscosity of aqueous solutions of the mono-, di- and dodecasubstituted sodium salts was studied at 20°.

7. The obtained results permit considering all of the obtained salts as being individual chemical compounds; it should also be mentioned that the investigated heteropoly compounds possess berthollide properties.

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COMPOSITION OF DIFFICULTLY SOLUBLE NICKEL COMPOUNDS PRECIPITATED BY ALKALI FROM SULFATE SOLUTION, AND THEIR STANDARD ISOBARIC POTENTIALS OF FORMATION

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It is known that nickel ions, as well as many other metallic ions, under the proper conditions form difficultly soluble hydroxides, basic salts and even more complex compounds. However, despite the large number of researches on the subject the composition and conditions for the formation of difficultly soluble nickel basic salts have not been established up to now. Thus, for example, Britton [1] found that 1.66 equivalents of alkali is required to precipitate all of the nickel from a 0.025 M solution, which fact is evidence that the basic salt is precipitated. On the other hand, Fialkov and Akselrud [2,3] consider the nature of their experimental results as being due to the formation of pure nickelous hydroxide in all of the concentration intervals studied by them. Rotinyan and Zeldes [4] showed that, at low concentrations of nickel sulfate in the potentiometric titration of the solution with alkali the pure nickelous hydroxide $Ni(OH)_2$ is formed, while at the same time for higher concentrations of $NiSO_4$ the solid phase consists of basic salts. Singley and Carriel [5] found that basic compounds are formed when nickel is precipitated by alkali from nickel chloride, nitrate, or sulfate solutions, these compounds with further elevation of the pH undergoing transition into the pure hydroxide.

According to the observation made by Bagno [6], the difficultly soluble nickel compound, precipitated from nickelous chloride solution by a mixture of NaOH and Na_2CO_3, undergoes a change in composition with time. The $CO_3^{=}$ ions, first found in the precipitate, are replaced by hydroxyl ions with the passage of time.

In the present study we set ourselves the task of establishing the composition of difficultly soluble nickel compounds, elucidate the conditions for their formation, and compute where possible the standard isobaric potentials for the formation of these compounds.

Selection of a method for determining the composition of the solid phase

The composition of the solid phase can be determined by several methods. At first glance, the most reliable composition of the solid phase is obtained by direct chemical analysis of the difficultly soluble compound, separated from its equilibrium solution. However, on closer examination this method very frequently proves to be inaccurate. Actually, if the solid phase is found in equilibrium with the solution only in a definite interval of salt activities and solution acidities, then on removing it from the mother liquor by washing with distilled water a change in the composition of the solid phase takes place toward the formation of a more basic compound. Consequently, this method is adaptable only in the case where constancy in the composition of the solid phase during washing has been established by some other independent method.

Another method [1] consists in the potentiometric determination of the amount of alkali necessary to precipitate all of the metal ions from solution. Calculation of the solid phase composition from the number of equivalents of alkali consumed for 1 equivalent of metal gives a true value only in the case where the precipitate retains a constant composition from the beginning to the end of the titration. Such a situation frequently fails to hold true in practice [7].

It is possible to determine the most trustworthy composition of the solid phase from the slope values for the relation pH vs. log metal salt activity in solution, with a large number of experimental points being plotted [7].

For this method it is necessary to know the pH values of the solutions in equilibrium with the solid phase at different salt activities. The hydrogen ion concentration in the solution found in equilibrium with the solid phase can be obtained by measuring the pH of the solution, brought to a state of visible turbidity by the addition of an alkaline reagent and held in order to attain equilibrium (Gromov • [8]).

• At low salt concentrations the method of Gromov has the disadvantage that a considerable portion of the salt may be lost in the formation of turbidity, and consequently its equilibrium concentration will be substantially different from the initial concentration, which concentration is used in the calculations.

The method of Akselrud and Fialkov [3], in accord with which the hydroxide (or basic salt) is precipitated separately, filtered and then brought into equilibrium with the salt solution (the equilibrium concentration of the salt is analyzed separately), gives the same physical value for the pH. Therefore, it is natural for the experimental data obtained by methods [3] and [8] to coincide with each other.

Other methods, by some means or other, fix the pH at the beginning of solid phase formation in the process of adding alkali to the solution. The initiation of solid phase formation can be detected by the inflection on either the potentiometric or conductometric titration curves, and also from polarographic measurement data [9,10].*

This group of methods usually requires fairly rapid experimental execution, as a result of which the solid phase may consist not of compounds in equilibrium with the solution but of difficultly soluble pseudoequilibrium compounds, for which the pH of formation differs from that of the equilibrium compounds.

The fact that the pH values determined by methods [8] and [3] at times are higher than the values obtained in the second group of methods is apparently due to the above situation.

To determine the composition of the solid phase we used in the present work the earlier described calculation method based on the slope coefficient values of the linear functions $pH - \log a_{\pm}$ [7]. To verify the obtained results we developed still another method for determining the composition of the deposited solid phase, based on measurement of the electrical conductivity of the coexistent solution. A detailed description of this method is given below.

EXPERIMENTAL

a) Measurement of the pH of formation of the hydroxide and basic salts of nickel by the potentiometric method. The pH values of the solutions coexisting with the solid phase were determined by both method [8] and by the potentiometric method [11].

It should only be emphasized that the potentiometric titration curves are taken in such a manner that each point is the result of measuring the established value of the electromotive force (change in e.m.f. < 1mV after 10-15 minutes). Reproducibility of the results was within ± 0.1 pH. The reagents used were carefully purified. Standard 0.1 N NaOH was used for the titrations.

The pH values corresponding to initial solid phase formation are given in the table. In the table are also given the pH values of the solutions in equilibrium with the solid phase, determined by the method of Bromov. These values for the coordinates $pH - \log a_{\pm}$ are depicted in Fig. 1. First of all it should be mentioned that the obtained results are in excellent agreement with the literatuare data [3,4], with the exception of the experiments performed by Gayer and Garrett [12], in which in dilute nickel chloride solutions the slope coefficient of the relation $pH - \log a_{\pm}$ proves to be 0.5 (i.e., the solid phase consists of pure nickel hydroxide, which agrees with our data) but the absolute pH values in their experiments are shifted by approximately a pH unit when compared with the values depicted in Fig. 1. Apparently, this divergence is caused by some systematic error hidden in the measurements of Gayer and Garrett. Further, it can be seen from Fig. 1 that at concentrations of nickel sulfate up to approximately 0.1 M the compound found in equilibrium with the solution (top curve) is the pure hydroxide (slope coefficient of the straight line is 0.5). At concentrations of nickel sulfate ranging from ~ 0.1 to ~ 1.0 the basic salt of composition $3NiSO_4 \cdot 4Ni(OH)_2$ is found in equilibrium with the solution. The composition of this basic salt is determined from the slope of the linear function $pH - \log a_{\pm}$ according to the formula

$$pH = \frac{\Delta Z^0_{basic}}{2.3nyRT} - \frac{y + bx + dx}{ny} \log a_{\pm} - \frac{1}{ny} \log \frac{b^{(y+bx)} d^{xd}}{\left(\frac{b}{b^{b+d}} \cdot \frac{d}{d^{d+b}}\right)^{y+bx+dx}} - \log K_w \qquad (1)$$

the derivation of which was given earlier [7].

(Here ΔZ^0_{basic} – standard isobaric potential of forming the basic salt in accord with the scheme:

$$(y + bx)\, Me^{n+} + dx\, A^{m-} + ny\, OH' \rightleftharpoons x[Me_bA_d]\, y[Me(OH)_n],$$

* The last method, recently proposed by Kovalenko, is to be preferred when the measurements are made in dilute solutions. Kovalenko determined the moment of initial hydroxide formation and the pH corresponding to it from the decrease in the metal diffusion current, taking a series of polarograms at different pH values.

If the titration is made, given the dropping mercury cathode diffusion potential, then the curve, constructed by Kovalenko from a number of polarograms, is obtained directly.

$a_{\pm}$ – mean salt activity in the solution, K_w – ionic product of water).

TABLE

The Influence of Nickel Sulfate Concentration on the pH of Solutions Coexisting with the Solid Phase

Nickel concentration		$\gamma_{\pm}$	$a_{\pm}$	pH potentiometrically determined at		pH determined by the method of Gromov at
g/liter	M			20°	50°	20°
0.10	0.0017	0.66	0.00112	7.94	7.04	7.66
0.15	0.0025	0.60	0.00150	7.90	6.86	7.87
0.20	0.0034	0.55	0.00187	7.85	6.82	7.78
0.30	0.0051	0.49	0.00249	7.77	6.80	7.70
0.40	0.0068	0.46	0.00309	7.58	6.68	7.62
0.49	0.0083	0.43	0.00355	–	–	7.53
0.50	0.0085	0.42	0.00361	7.61	6.62	7.63
0.60	0.0102	0.40	0.00413	7.58	6.45	7.56
0.70	0.0119	0.38	0.00458	7.44	6.56	7.56
0.80	0.0136	0.37	0.00503	7.36	6.52	7.55
0.90	0.0153	0.35	0.00543	7.34	6.46	7.48
0.96	0.0163	0.34	0.00562	–	–	7.48
1.0	0.0170	0.34	0.00578	7.24	6.42	7.52
1.0	0.0170	0.34	0.00578	–	–	7.38
1.5	0.0255	0.29	0.00739	7.10	6.38	–
1.88	0.0320	0.26	0.00848	–	–	7.38
2.0	0.0341	0.26	0.00886	7.08	6.32	7.30
2.14	0.0364	0.26	0.00937	–	–	7.38
3.0	0.0511	0.23	0.01175	6.92	–	–
5.0	0.0852	0.18	0.01533	6.78	5.94	7.28
10	0.1704	0.12	0.02044	6.51	5.70	7.17
20	0.3408	0.075	0.02556	6.41	5.36	6.98
30	0.5146	0.065	0.03345	6.15	5.16	6.88
40	0.6815	0.055	0.03748	6.10	5.14	6.77
50	0.8519	0.050	0.04259	6.04	4.98	6.72
60	1.0223	0.045	0.04600	5.84	4.94	6.67

b) Study of the composition of basic salts by the electrical conductivity method. We will examine the case where the addition of alkali to a nickel sulfate solution results in the formation of a difficultly soluble compound in accord with the reaction

$$(x + y)\,NiSO_4 + 2yNaOH = x\,NiSO_4 \cdot yNi(OH)_2 + yNa_2SO_4. \qquad (2)$$

To perform the experiment we chose such concentrations of salt and alkali that, first, the conductivity of the mixed solution as a first approximation was additively composed of the conductivities of the individual component solutions and, second, that in the selected concentration interval the change in the specific conductance of the solution was proportional to the salt concentration.

With progress of reaction (2) the conductivity of the solution should drop due to decrease in nickel sulfate concentration and simultaneously it should rise due to the formation of sodium sulfate. The change in the specific conductance of the solution during solid phase formation is influenced by both factors.

If the experiment is conducted in such a manner that to a constant volume of nickel sulfate solution of concentration C_1 there is added V ml of alkali solution of concentration C_2, the solution made up to constant volume W with distilled water, next filtered and the specific conductance of the filtrate determined, then, in accord with the equation for the reaction, the change in nickel sulfate concentration is expressed by

$$\Delta C_1 = \frac{\Delta(C_2V)}{W}\,\frac{(x+y)}{2y}\,. \qquad (3)$$

Here C_1 and C_2 are expressed in moles per milliliter.

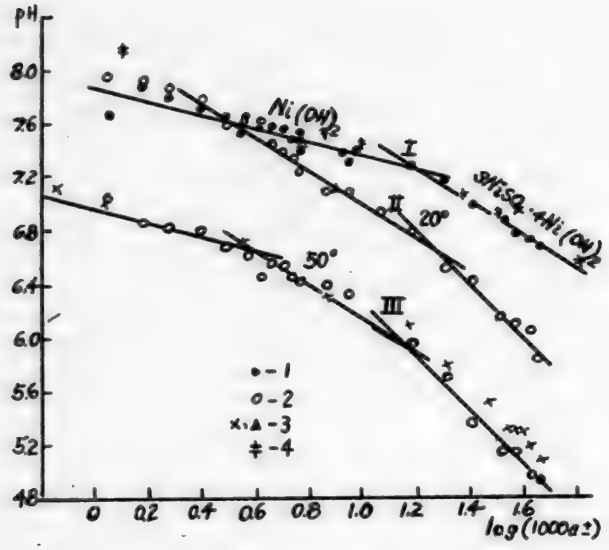

Fig. 1. Relation of the pH of initial solid phase formation vs. the logarithm of nickel sulfate activity in solution.

1) Our data at 20°, obtained by the Gromov method; 2) our data, obtained from the potentiometric titration curves at 20° and 50°; 3) data of Rotinyan and Zeldes at 50° [4] and at 20° [11]; 4) data of Akselrud and Fialkov [3].

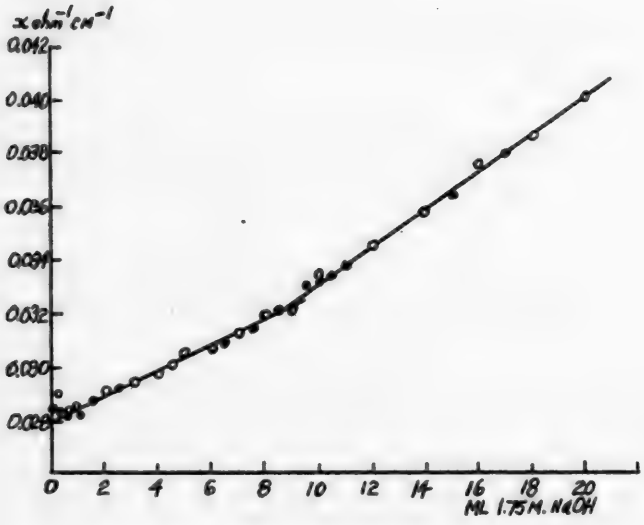

Fig. 3. Change in the specific conductance of the solution during the precipitation of nickel from sulfate solution with alkali.

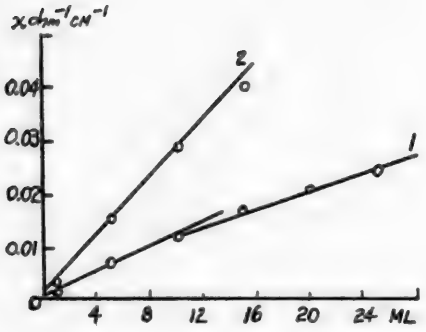

Fig. 2. Change in the specific conductance of nickel and sodium sulfate solutions with change in concentration.

1) Relation between the specific conductance of nickel sulfate solution and salt concentration, expressed in milliliters of 0.681 M $NiSO_4$ solution in 50 ml of solution, 2) Analogous curve for sodium sulfate; initial concentration of $NaSO_4$ solution 1 M.

When the above indicated conditions are observed in the experiment the change in the specific conductances of nickel and sodium sulfates will be:

$$\Delta \kappa_{NiSO_4} = -K_1 \Delta C_1 = -K_1 \frac{\Delta (C_2 V)}{W} \frac{(x+y)}{2y}; \quad (4)$$

$$\Delta \kappa_{Na_2SO_4} = K_2 \frac{\Delta (C_2 V)}{2W}. \quad (5)$$

Consequently, the total change in conductivity will be determined by the expression

$$\Delta \kappa_{\Sigma} = \frac{\Delta (C_2 V)}{2W} \left[K_2 - K_1 \frac{(x+y)}{y} \right], \quad (6)$$

from which it is seen that the change in the specific conductance of the solution during precipitation of the basic salts or hydroxides should as a first approximation be proportional to the amount of added alkali. In other words, the relation $\kappa_{\Sigma} - C_2 V$ should be expressed by a straight line in the whole concentration interval for the original salt in which a precipitate of constant composition is obtained.

With changes in the composition of the precipitate the indicated straight line will suffer breaks.

The tangent to the slope of each straight portion is equal to

$$\frac{\Delta \kappa_{\Sigma}}{\Delta (C_2 V)/2W} = K_2 - K_1 \frac{(x+y)}{y}. \quad (7)$$

Equation (7) makes if possible to determine the composition of the precipitate (values x and y) from the slope of the linear function $\kappa_{\Sigma} - C_2V$, provided constants K_1 and K_2 are known.

The latter are determined from the individual conductivity measurements of pure nickel sulfate and sodium sulfate solutions at different concentrations. 0.681 M Nickel sulfate solution and 1.000 M sodium sulfate solution were used to determine the constants K_1 and K_2. Both salts were carefully purified beforehand.

The different amounts of salt solution were made up to 50 ml with distilled water, after which the electrical conductivity of the solution was determined with the aid of the ordinary bridge scheme. The determination results are given in Fig.2, from which it can be seen that under experimental conditions the change in specific conductance with change in concentration is indeed linear.

Inasmuch as constants K_1 and K_2 denote the change in the specific conductance of $NiSO_4$ and Na_2SO_4 solutions with unit change in concentration, then evidently

$$K_1 = \frac{\Delta \kappa_{NiSO_4}}{\Delta C_{NiSO_4}} \text{ and } K_2 = \frac{\Delta \kappa_{Na_2SO_4}}{\Delta C_{Na_2SO_4}}. \quad (8)$$

We started with a solution of nickel sulfate in our experiments. Consequently, for calculating K_1 in the initial experimental stages it is necessary to take the slope coefficient of the straight line corresponding to the higher concentrations of nickel sulfate, while for calculating K_2 it is necessary to use the values corresponding to low concentrations of sodium sulfate.

The calculation of constants K_1 and K_2 under these conditions gives:

$$K_1 = \frac{8.3 \cdot 10^{-4} \cdot 50 \cdot 1000}{0.681} = 61.8$$

$$K_2 = \frac{26.5 \cdot 10^{-4} \cdot 50 \cdot 1000}{1} = 132.5.$$

At low concentrations of nickel sulfate

$$K_1 = \frac{11.5 \cdot 10^{-4} \cdot 50 \cdot 1000}{0.681} = 84.4$$

A number of solutions were prepared for the nickel precipitation experiments, the solutions containing 25 ml of 1 M $NiSO_4$ and various amounts of 1.75 M NaOH; after this the solutions were made up to 50 ml. The solutions were filtered and the specific conductances were determined at 20°, either on the following day or immediately. The results of two parallel experiments, in which the solutions were filtered and the specific conductances determined on the second day after precipitation of the nickel with alkali, are given in Fig. 3. The starting solution was acidified slightly, as a result of which the first portions of alkali were consumed in neutralizing the excess acidity and the specific conductance dropped. From Fig. 3 it can be seen that the obtained data arrange themselves along two linear sections.

The slope coefficient corresponding to the higher concentrations of nickel sulfate is

$$\frac{4.4 \cdot 10^{-4} \cdot 10 \cdot 1000}{1.75} = 25.1,$$

while for more dilute solutions it is

$$\frac{7.1 \cdot 10^{-4} \cdot 10 \cdot 1000}{1.75} = 40.5$$

The values x and y are determined from these slope coefficient values and the constants K_1 and K_2.

For the first section $x = 0.74\ y$, while for the second,* $\frac{x+y}{y} = 1.09$, i.e., as an approximation $x = 0$ and $y = 1$.

*In calculating the composition of the solid phase in this case $K_1 = 84.4$ and $K_2 = 132.5$. The last constant was used on the assumption that it is valid up to fairly high concentrations of sodium sulfate.

As a result, from the conductivity measurements it follows that the precipitate corresponding to the first section of the curve in Fig. 3 has the composition $3NiSO_4 \cdot 4Ni(OH)_2$, while the second section corresponds to $Ni(OH)_2$.

The experiments in which the precipitate was not allowed to stand with the solution gave analogous results, and consequently are not presented here.

The developed method has the advantage that it permits determining the composition of the precipitated compound, even if the latter is not found in equilibrium with the solution, whereas the determination method based on the slope of the linear function $pH - \log a_{\pm}$ assumes that the solid phase is in equilibrium with the solution.

DISCUSSION OF RESULTS

First of all it should be mentioned that the slope coefficient and electrical conductivity methods are in excellent agreement as regards the composition values obtained for the solid phase. Both the calculations according to Equation (1) and the conductivity method lead to the conclusion that in dilute solutions pure nickelous hydroxide is formed, whereas in more concentrated solutions the basic salt $3NiSO_4 \cdot 4Ni(OH)_2$ is precipitated.

Basic conclusions may be derived from a comparison of the results obtained by the "equilibrium" method of Gromov and the "rapid" potentiometric titration method. If the data obtained with these methods agree with each other at low concentrations of nickel sulfate, then significant and regular differences exist in more concentrated solutions.

The conductivity method shows that in the case of rapid titration the composition of the precipitate is such that it is in equilibrium with a more concentrated nickel sulfate solution.

This circumstance makes it possible to interpret the data of the potentiometric titration method.

Specifically, from Fig. 1 it follows that at low salt concentrations the pure nickelous hydroxide is formed, and then, insofar as the solid phase in all cases is in equilibrium with the solution, the pH values obtained from the potentiometric titration curves and by the Gromov method coincide with each other. In more concentrated nickel sulfate solutions the basic salt is formed during titration, which only after a long period of time is transformed into pure nickelous hydroxide (cf. left section of Curve II).

The composition of the pseudoequilibrium compound under the given conditions corresponds to $3NiSO_4 \cdot 4Ni(OH)_2$, i.e., it corresponds to the composition of the basic salt found in equilibrium with the solution in the region of higher nickels sulfate activities. It should be mentioned that the slope coefficient for this section of Curve II (Fig. 1) is equal to the slope coefficient of the extreme right section of equilibrium Curve I.

At even higher nickel sulfate concentrations the first precipitated basic salt has a less basic character than before, which with the passage of time is transformed not into the pure hydroxide but instead into a more basic salt, namely $3NiSO_4 \cdot 4Ni(OH)_2$.

If the composition of the second pseudoequilibrium salt is calculated from the slope coefficient of Curve II (right section), then it corresponds to the formula $3NiSO_4 \cdot 2Ni(OH)_2$.

Under equilibrium conditions this salt is probably formed at extremely high nickel sulfate activities, which activities were not attained in our experiments; consequently, on the equilibrium Curve I the section with the same slope coefficient is not shown.

Curve III (Fig. 1), obtained by the potentiometric method at 50°, shows that the slope coefficients remain constant when the temperature is raised. This condition serves as evidence that the same difficultly soluble compounds are formed at 50° and at room temperature.

It should also be mentioned that our data are in satisfactory agreement with the earlier obained values [4].

On the basis of the obtained data, it may be concluded that in general the potentiometric titration method, as well as the other "rapid" methods for determining the pH at the beginning of solid phase formation, do not give the right to calculate the free energy of formation of the salt.

In conclusion, we wish to state that the possibility of forming pseudoequilibrium compounds limits even more the practical use of the so-called pH series for the precipitation of hydroxides [1,2], for the solution of concrete problems is governed, not by the equilibrium pH values existing at the beginning of solid phase formation, but by those pH values that are established under the given process rate.

Calculation of the standard isobaric potentials on the basis of the equilibrium curve leads to the following values.

The standard isobaric potential for the formation of nickelous hydroxide from the ions is −20.8 kcal/ mole, whereas the value −18.9 kcal/ mole was obtained earlier.

The standard isobaric potential for the formation of the basic salt $3NiSO_4 \cdot 4Ni(OH)_2$ (ΔZ^0_{basic}) is −96.0 kcal for 1 mole of basic salt and the standard isobaric potential for the addition of 3 moles of nickel sulfate to 4 moles of nickelous hydroxide ($\Delta Z^0_{addn.}$) is −20.4 kcal for 1 mole of basic salt.

SUMMARY

1. The method of analyzing the equilibrium curves pH − log $a^{\pm}$ was used to determine the compositions of difficultly soluble nickel salts formed in the treatment of $NiSO_4$ solutions with alkali solutions.

2. The obtained results were verified by the method of analyzing the conductivity curves for the mother liquors during the precipitation of basic nickel salts with alkali.

3. It was shown that at low nickel sulfate activities the pure hydroxide is formed, while at higher activities the basic salt $3NiSO_4 \cdot 4Ni(OH)_2$ is formed. The standard isobaric potentials for the formation of these compounds were calculated, as was also the standard isobaric potential for the addition of nickel sulfate to nickelous hydroxide with the formation of $3NiSO_4 \cdot 4Ni(OH)_2$.

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Received March 19, 1954.

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BINARY SYSTEM RUBIDIUM SULFATE-MAGNESIUM SULFATE

V. E. Plyushchev and N. F. Markovskaya

Insofar as we know, the binary system of rubidium and magnesium sulfates has not been studied.

Only the formation of the binary sulfates of rubidium and magnesium, $Rb_2SO_4 \cdot MgSO_4$ and $Rb_2SO_4 \cdot 2MgSO_4$ is indicated in the literature. According to the data of Mallet [1,2], both compounds can be obtained by cooling a melt of the anhydrous components taken in the proper proportions. The compound $Rb_2SO_4 \cdot 2MgSO_4$ is an analog of langbeinite and possesses identical properties.

EXPERIMENTAL

In our work the system $Rb_2SO_4-MgSO_4$ was studied by the melting point method, a pyrometer of the Kurnakov type being used to record the cooling (heating) curves. The Pt-PtRh thermocouple was mounted in combination and was calibrated from the transition and melting points of chemically pure $Na_2SO_4 \cdot 10\,H_2O$, Na_2SO_4, K_2SO_4, and also from the melting points of $K_2Cr_2O_7$, NaCl, and eutectic in the system Na_2SO_4-NaCl.

As a rule, the melts were prepared with 5% increment changes in the composition; some sections of the fusion diagram, as can be seen from the table, were studied in greater detail. The starting salts used in studying the system were chemically pure Rb_2SO_4 and $MgSO_4 \cdot 7H_2O$, anhydrous magnesium sulfate being obtained from the latter.

The purity of these sulfates was verified by spectral analysis.

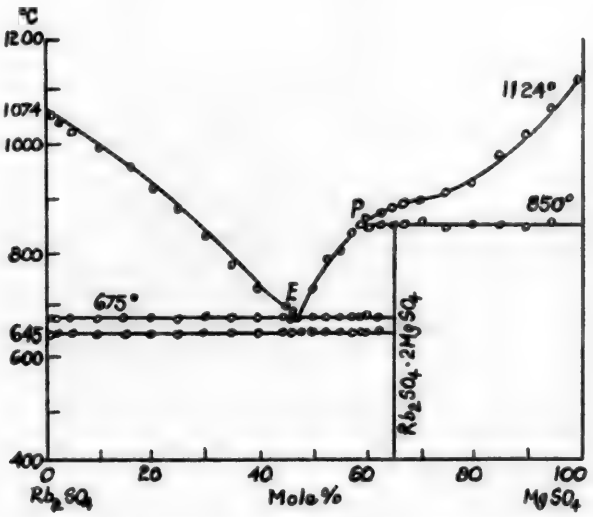

Fig. Melting-point diagram of the system rubidium sulfate - magnesium sulfate

The presence of a eutectic point in the melts with a high $RbSO_4$ content leads to the conclusion that solid solutions are not formed on a rubidium sulfate base, at least not in the region of investigated concentrations. Also, solid solutions were not revealed in the region of high magnesium sulfate concentrations.

The system has two characteristic points – the transition point (P) and the eutectic (E). The first, corresponding to 59 mole % $MgSO_4$, reflects the existence in the system of the compound melting with decomposition at 850°. The maximum duration of the halts at 850° is observed in the case of the melt containing 66.7 mole % $MgSO_4$. This circumstance permits assigning to the compound the formula $Rb_2SO_4 \cdot 2MgSO_4$. The existence of the compound is confirmed by the character of the thermal diagram for the melts and by X-ray phase analysis.

No other compounds are present in the system. The eutectic, formed from α-Rb_2SO_4 and compound, corresponds to 675° and 47.5 mole % $MgSO_4$.

The cooling (heating) curves of the melt containing 47.5 mole % $MgSO_4$, having only two temperature halts responding to the eutectic line and the conversion of α-Rb_2SO_4 into β-Rb_2SO_4, demonstrate the presence of a eutectic.

The derived conclusions on the character of the system are confirmed by the microstructure of the melts.

TABLE

$MgSO_4$ (in mole %)	Temperature			
	Polymorphic transformation of Rb_2SO_4	Eutectic	Formation of compound $Rb_2SO_4 \cdot 2MgSO_4$	Melting point
0.0	645°	–	–	1074°
1.0	645	676°	–	1058
2.5	646	675	–	1040
5.0	643	677	–	1026
10.0	645	672	–	995
15.0	645	675	–	955
20.0	648	675	–	918
25.0	645	672	–	882
30.0	645	678	–	830
35.0	648	675	–	775
40.0	645	675	–	728
45.0	645	673	–	700
46.5	645	675	–	685
47.5	645	675	–	675
50.0	648	675	–	728
52.5	648	675	–	785
55.0	642	675	–	800
57.5	645	678	–	830
59.0	645	675	850°	850
60.0	645	675	850	860
62.5	645	675	850	870
65.0	–	–	850	880
66.7	–	–	850	890
70.0	–	–	853	898
75.0	–	–	847	910
80.0	–	–	850	930
85.0	–	–	848	975
90.0	–	–	846	1015
95.0	–	–	850	1065
100.0	–	–	–	1124

It should be mentioned that in the literature the melting point values given for $MgSO_4$ differ considerably, due to decomposition of the latter during fusion. However, with rapid and vigorous heating it is possible to obtain concordant results. According to our data magnesium sulfate melts at 1124°. As a result, the binary system Rb_2SO_4–$MgSO_4$ belongs to the type of system with unlimited miscibility of the components in the molten state and crystallization of a chemical compound melting with decomposition.

SUMMARY

1. The thermal analysis method was used to study the binary system

Rb_2SO_4–$MgSO_4$.

2. The existence in the system of a compound having the composition $Rb_2SO_4 \cdot 2MgSO_4$ and melting with decomposition was established.

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Received February 16, 1954.

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DOUBLE DECOMPOSITION IN THE ABSENCE OF SOLVENT

I. QUATERNARY RECIPROCAL SYSTEM OF LITHIUM AND POTASSIUM CHLORIDES, SULFATES AND TUNGSTATES

A. G. Bergman, A. I. Kislova and V. I. Posypaiko

The study of metallic tungstates in melts attracts the natural and deserved interest of investigators. We studied a number of ternary reciprocal systems in which lithium and potassium tungstates were present [1]. An even more interesting problem is the behavior of these tungstates in the make-up of a complex multicomponent system - the quaternary reciprocal system Li, K | Cl, SO_4, WO_4. The visual-polythermal method [2] was used to study the given system.

EXPERIMENTAL

The system studied by us, in the form of a triangular prism [3] (Fig. 1), has at the apexes the components with the following melting points Li_2Cl_2 606°, Li_2SO_4 860°, Li_2WO_4 738°, K_2Cl_2 774°, K_2SO_4 1069°, K_2WO_4 926°. Lithium chloride differed from the other salts in being extremely hydroscopic, which required constant drying of the salt and determination of its weight by difference from the box. Nearly all of the components are characterized by transformation points at different temperatures. Thus, it was established: for lithium chloride homeomorphic transformation at 565° [4], for potassium chloride at 27 and 384° [5], for lithium sulfate heteromorphic transformation at 572° [6], for lithium tungstate heteromorphic transformation at 660° [7].

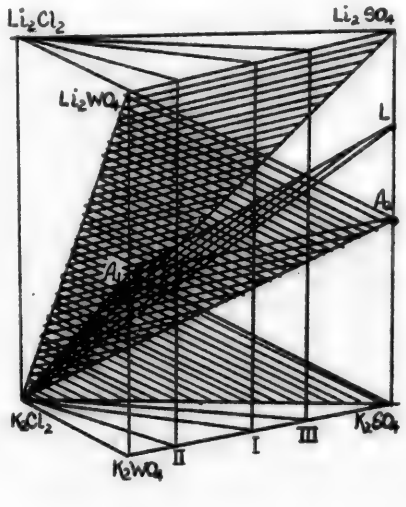

Fig. 1. Section scheme through the quaternary reciprocal system Li, K ‖ Cl, SO_4, WO_4.

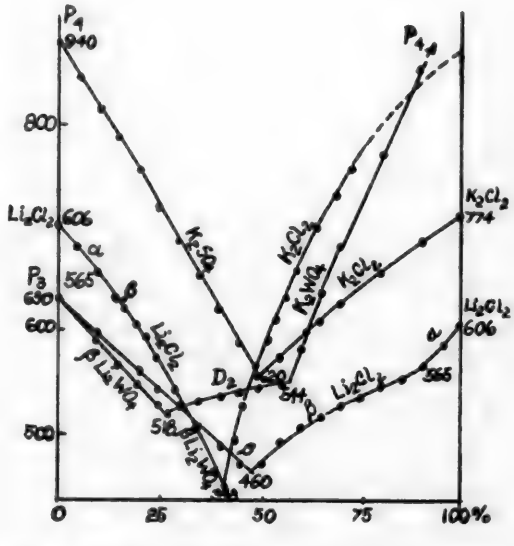

Fig. 2. Sides of book section I.

The results of our studies on the base of the prism – the ternary systems K ‖ Cl, SO_4, WO_4 and Li ‖ Cl, SO_4, WO_4, and also of the sides of the prism – the ternary reciprocal systems Li, K ‖ Cl, WO_4 and Li, K ‖ SO_4, WO_4 • – are being published in separate papers.

• The third side of the given prism – the ternary reciprocal system Li, K ‖ Cl, SO_4 – was studied by Dombrovskaya [8] and later by Bergman and Akopov. We used the data of the latter authors.

For the complete study of the internal structure of this prism there were taken three book and five internal triangular sections through the composition prism(Fig. 1).

The results of studying the book sections are briefly described below.

Book Sections of the Quaternary Reciprocal System Li, K ‖ Cl, SO_4, WO_4

The book sections were conditionally taken and studied as ternary reciprocal systems depicted in the form of rectangles. The following sections are to be found in the composition prism.

TABLE 1

Binary Systems

P_3-P_4*		$P_3-Li_2Cl_2$		$P_4-K_2Cl_2$		$Li_2Cl_2-K_2Cl_2$	
% P_4	Temperature	% P_3	Temperature	% K_2Cl_2	Temperature	% K_2Cl_2	Temperature
0	630°	0	606°	0	940°	0	606°
10	590	10	565	10	878	10	560
20	544	20	542	20	816	20	510
25	525	30	526	30	750	30	448
27.5	518	40	504	40	685	40	368
30	524	45	490	45	650	45	462
40	535	50	468	50	620	50	472
50	512	52.5	460	55	636	55	516
55	544	55	468	60	650	60	564
57.5	544	60	485	70	688	65	604
60	578	70	524	80	718	70	638
70	680	80	558	90	750	75	664
80	772	100	630	100	774	80	690

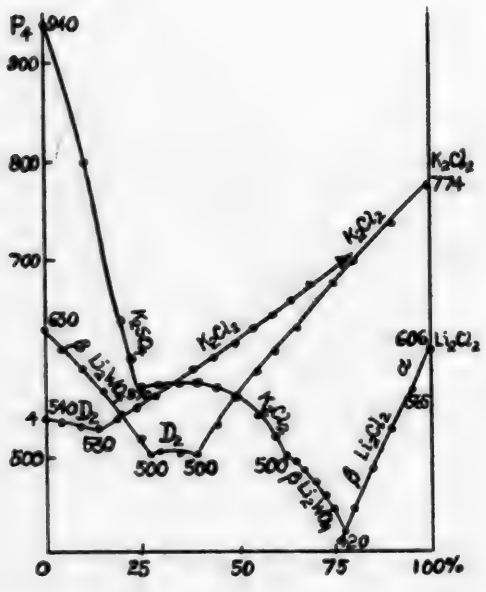

Fig. 3. Curves of Section I.

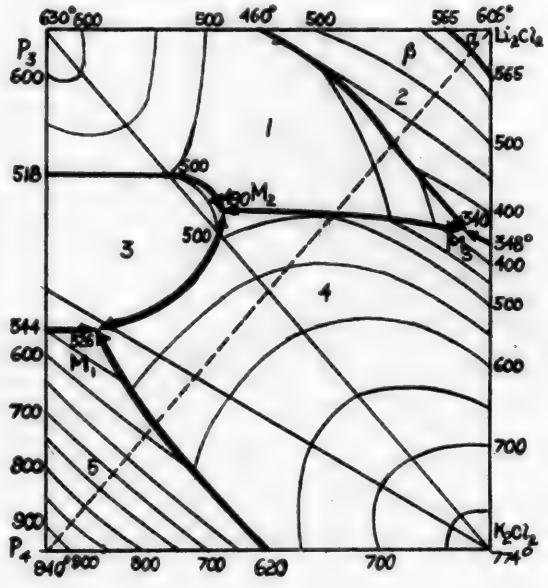

Fig. 4. Section I. 1) β-Li_2WO_4, 2) Li_2Cl_2, 3) $Li_2SO_4 \cdot K_2SO_4$, 4) K_2Cl_2, 5) K_2SO_4.

* We will conditionally designate: (50% Li_2WO_4 + 50% Li_2SO_4) by P_3, and (50% K_2WO_4 + 50% K_2SO_4) by P_4.

TABLE 2

Diagonal				Internal Section (50 % P_3 50% P_4)−K_2Cl_2	
$P_3-K_2Cl_2$		$P_4-Li_2Cl_2$			
% K_2Cl_2	Temperature	% P_4	Temperature	% K_2Cl_2	Temperature
0	630°	0	606°	0	540°
10	590	10	528	5	537
20	544	20	445	10	535
25	518	22.5	420	15	530
27.5	500	25	445	20	540
30	503	35	495	25	552
35	503	37.5	500	30	565
40	500	40	520	35	580
45	530	50	560	40	592
50	560	60	572	45	605
60	605	70	574	50	620
70	650	77.5	600	60	645
80	696	80	640	70	678

Book section I (50% Li_2WO_4 + 50% Li_2SO_4)−(50% K_2WO + 50% K_2SO_4)−Li_2Cl_2−K_2Cl_2.

The sides of the rectangle are the sections (Table 1, Fig. 2): *

1) (50% Li_2WO_4 + 50% Li_2SO_4)−(50% K_2WO_4 + 50% K_2SO_4) ** − branches β-Li_2WO_4, $Li_2SO_4 \cdot K_2SO_4$, *** P_4 intersect at 518° and 27.5% P_4, 544° and 57.7% P_4.

2) (50% Li_2WO_4 + 50% Li_2SO_4)−Li_2Cl_2 − branches Li_2Cl_2 and P_3 intersect at 460° and 52.5% P_3. Branch Li_2Cl_2 is complicated by homeomorphic transformation at 565° and 10% P_3.

3) (50% K_2WO_4 + 50% K_2SO_4)−K_2Cl_2− branches P_4 and K_2Cl_2 intersect at 620° and 50% K_2Cl_2.

4) Li_2Cl_2−K_2Cl_2 was first studied by Zhemchuzhnyi and Rambakh [9].

We repeated our study of the system liquidus and the existence of a eutectic at 348° and 42% K_2Cl_2 was established. Homeomorphic transformation was noted on the Li_2Cl_2 branch at 565°.

Diagonal Sections (Table 2, Figure 3)

1) (50% Li_2WO_4 + 50% Li_2SO_4)−K_2Cl_2 have three branches: β-Li_2WO_4, $Li_2SO_4 \cdot K_2SO_4$, K_2Cl_2, intersecting at 500° and 27.5 % K_2Cl_2, 500° and 40% K_2Cl_2.

2) (50% K_2WO_4 + 50% K_2SO_4)−Li_2Cl_2 has four branches: β-Li_2Cl_2, β-Li_2WO_4, K_2Cl_2 and K_2SO_4, intersecting at 420° and 22.5% P_4, 500° and 37.5% P_4, 570° and 76% P_4. Polymorphism is observed on the Li_2Cl_2 branch at 565° and 5% P_4.

Internal section (50% P_3 + 50% P_4)−K_2Cl_2 (Table 2, Fig. 3), branches K_2Cl_2 and $Li_2SO_4 \cdot K_2SO_4$ meet in the transition point at 530° and 15% K_2Cl_2.

A number of cuts **** through the rectangle made it possible to study with sufficient accuracy the surface of crystallization of the given section through the quaternary reciprocal system (Fig. 4).

The compositions and temperatures of the univariant points in the system are given below in Table 3.

The surface of crystallization of the section is broken up into five fields, of which one is the field of the binary compound 1:1 $Li_2SO_4 \cdot K_2SO_4$, while the remaining are fields of the components.

The calculated areas of the crystallization fields, expressed in area per cent of the rectangle, are: α-Li_2Cl_2−0.6, β-Li_2Cl_2−9.6, β-Li_2WO_4−23.4, K_2SO_4−12.3, K_2Cl_2−43.42, $Li_2SO_4 \cdot K_2SO_4$−10.68%.

* Only the more important points are indicated in the tables. All of the points are given in the figures.

** We will conditionally designate: (50% Li_2WO_4 + 50% Li_2SO_4) by P_3, and (50% K_2WO_4 + 50% K_2SO_4) by P_4.

*** We will designate the compound $Li_2SO_4 \cdot K_2SO_4$ by D_2.

**** In all three book sections 10 cuts per section were made through the surface of crystallization. Due to the voluminous nature of the material the curves and tables of all of these cuts are not given in this paper.

TABLE 3

Point	Temperature	Composition (in mole %)				Equilibrium phases
		K_2Cl_2	P_3	P_4	Li_2Cl_2	
M_1	526°	10	42	48	–	K_2SO_4, D_2, K_2Cl_2.
M_2	490	–	24	35	41	Li_2WO_4, D_2, K_2Cl_2.
M_3	340	38.4	6	–	55.5	Li_2WO_4, K_2Cl_2, Li_2Cl_2.

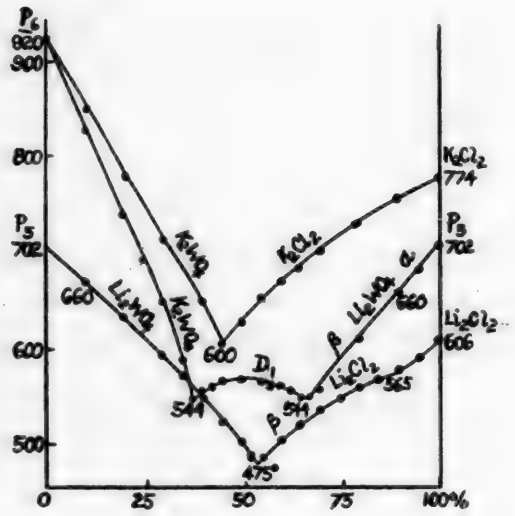

Fig. 5. Sides of Book Section II.

As a result, the given section establishes the fact that the complex compound $Li_2SO_4 \cdot K_2SO_4$, melting without decomposition, retains its stability also inside the system. Characteristic are the planar form of the complex and almost the complete absence of isotherms.

Complex formation is the predominant reaction in the system.

Book Section II (80% Li_2WO_4 + 20% Li_2SO_4) – (80% K_2WO_4 + 20% K_2SO_4) – Li_2Cl_2 – K_2Cl_2.

The rectangle is composed of the following sections (Table 4, Fig. 5):

1) (80% Li_2WO_4 + 20% Li_2SO_4) – (80% K_2WO_4 + 20% K_2SO_4)* branches: Li_2WO_4, compound $Li_2WO_4 \cdot K_2WO_4$** intersect at 544° and 33% P_6, 544° and 62.5% P_6. Branch Li_2WO_4 at 660° and 10% P_6 is complicated by polymorphic transformation.

2) (80% Li_2WO_4 + 20% Li_2SO_4) – Li_2Cl_2 – branches P_5 and Li_2Cl_2 intersect at 475° and 46.5% P_5. Homeomorphic transformation is observed on branch Li_2Cl_2 at 565° and 15% P_5. Branch Li_2WO_4 separates into the α - and β -modifications at 660° and 87.5 %. P_5.

3) (80% K_2WO_4 + 20% K_2SO_4) – K_2Cl_2 – branches K_2Cl_2 and K_2WO_4 intersect at 600° and 45% K_2Cl_2.

4) Li_2Cl_2 – K_2Cl_2 – eutectic at 358° and 42% K_2Cl_2 (Table 1, Fig. 2).

TABLE 4
Binary System

P_5 – P_6		P_6 – K_2Cl_2		P_5 – Li_2Cl_2	
% P_6	Temperature	% K_2Cl_2	Temperature	% P_5	Temperature
0	702°	0	920°	0	606°
10	660	10	846	10	575
20	606	20	774	15	564
30	550	30	710	20	566
32.5	546	40	646	30	532
35	546	45	600	40	500
40	556	50	624	45	482
45	560	55	648	47.5	482
50	565	60	665	50	500
55	562	65	680	55	520
60	552	70	698	60	544
62.5	544	80	725	70	590
65	584	90	750	80	628
75	690	100	774	90	665

* For convenience we will designate the composition (80% Li_2WO_4 + 20% Li_2SO_4) by P_5, (80% K_2WO_4 + 20% K_2SO_4) by P_6.

** For convenience we will designate the compound 1:1 $Li_2WO_4 \cdot K_2WO_4$ by D_1.

Diagonal Sections (Table 5, Figure 6)

1) P_5—K_2Cl_2— intersection of branches P_5 and K_2Cl_2 at 522° and 42% K_2Cl_2. Polymorphism of Li_2WO_4 was observed at 660° and 6.5% K_2Cl_2.

2) P_6—Li_2Cl_2— branches Li_2Cl_2, β -Li_2WO_4, K_2Cl_2, K_2WO_4 intersect at 438° and 20% P_6; 545° and 45% P_6; 545° and 78% P_6.

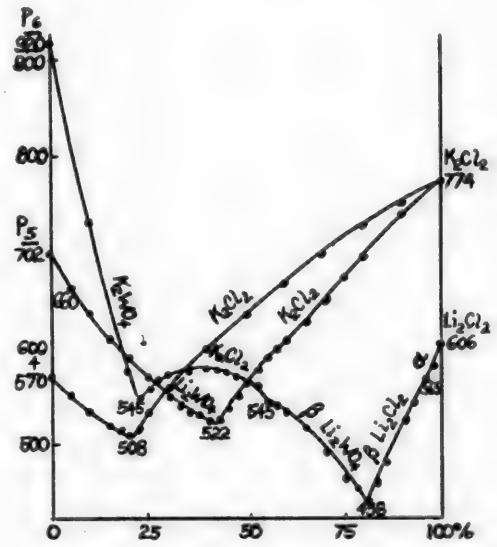

Fig. 6. Curves of Section II.

Polymorphism was observed on branch Li_2Cl_2 at 565° and 5% P_6. Internal section (50% P_5 + 50% P_6)—K_2Cl_2 (Table 5, Fig. 6), two branches intersect at 508° and 21% K_2Cl_2.

A study of a number of sections through the given rectangle made it possible to depict with the necessary accuracy the surface of crystallization of this book section through the quaternary composite system (Fig. 7). It consists of five fields, representing in per cent to the total area of the rectangle: K_2Cl_2—40.1, K_2WO_4—9.9, field of the compound 1 : 1 $Li_2WO_4 \cdot K_2WO_4$—9.9, α - and β -$LiWO_4$—31, α - and β -Li_2Cl_2— 9.1%.

The crystallization fields converge into three univariant points, the compositions and temperatures of which are given in Table 6.

The field of compound 1 : 1 $Li_2WO_4 \cdot K_2WO_4$ has a planar form and is characterized by the absence of isotherms. Being a compound that melts without decomposition, it retains its stability inside the section and quite deeply dislodges the fields of the components.

The lithium tungstate field, having an elongated form, separates into α - and β -portions. The isotherms of the potassium chloride field are characterized by a convex shape, becoming somewhat flatter when the temperature is lowered. In the lithium chloride field sections of homeomorphic transformations were also observed. Finally, the potassium tungstate field is characterized by steep slope isotherms with frequent decomposition. Complex formation is the predominant reaction in the system.

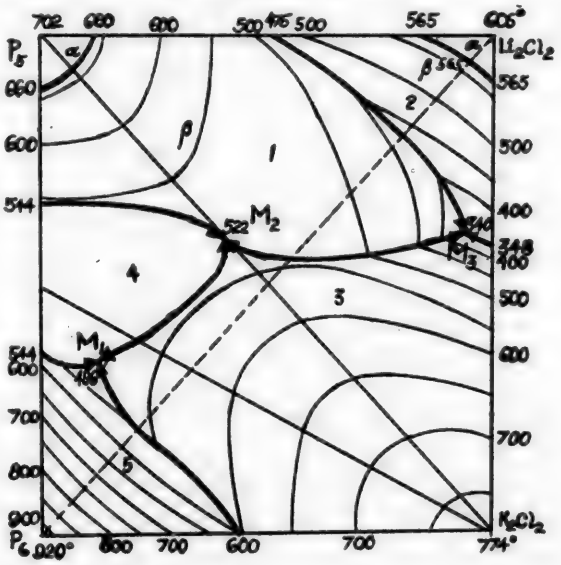

Fig. 7. Section II.
1) Li_2WO_4, 2) $LiCl_2$, 3) K_2Cl_2, 4) $Li_2WO_4 \cdot K_2WO_4$, 5) K_2WO_4.

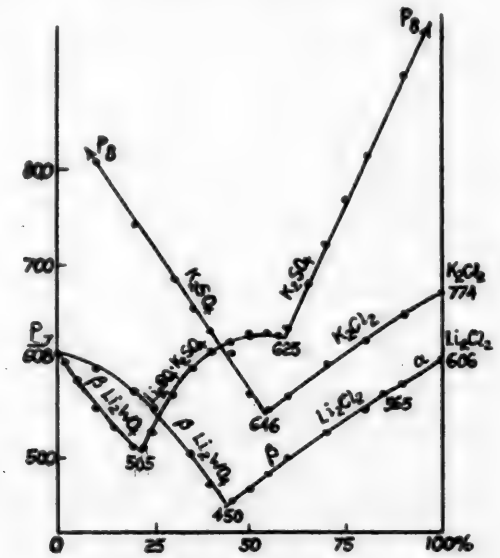

Fig. 8. Sides of Book Section III.

Book Section III ($30\%\ Li_2WO_4 + 70\%\ Li_2SO_4$)–($30\%\ K_2WO_4 + 70\%\ K_2SO_4$)–$Li_2Cl_2$–$K_2Cl_2$.

The following sections compose the rectangle of the given book section (Table 7, Fig. 8):

TABLE 5

Diagonal				Section	
P_5–K_2Cl_2		P_6–Li_2Cl_2		(50 % P_5 + 50% P_6)–K_2Cl_2	
% K_2Cl_2	Temperature	%P_6	Temperature	% K_2Cl_2	Temperature
0	702°	0	606°	0	570°
10	638	2.5	580	5	550
20	590	5	565	10	535
30	550	7.5	545	15	520
35	535	10	525	17.5	515
37.5	530	17.5	460	22.5	516
40	525	20	438	25	530
42.5	525	25	465	30	560
45	538	35	518	40	600
47.5	550	45	545	50	635
50	565	50	565	60	666
70	648	60	578	70	700
80	698	70	575	80	728
90	740	77.5	548	90	750
–	–	80	576	–	–

TABLE 6

Point	Temperature	Composition (in mole%)				Equilibrium phases
		K_2Cl_2	P_5	P_6	Li_2Cl_2	
M_1	496°	11.5	37	51.5	–	K_2WO_4, D_1, K_2Cl_2.
M_2	522	41.5	58.5	–	–	D_1, Li_2WO_4, K_2Cl_2.
M_3	340	40	7.5	–	52.5	Li_2WO_4, Li_2Cl_2, K_2Cl_2.

TABLE 7

Binary System

P_7–P_8		P_8–K_2Cl_2		P_7–Li_2Cl_2	
% P_8	Temperature	% P_8	Temperature	% P_7	Temperature
0	608°	0	774°	0	606°
10	552	10	750	10	576
20	512	20	726	20	550
22.5	512	30	697	30	525
30	566	40	665	40	500
40	610	45	650	50	467
50	625	50	667	55	455
57.5	627	55	710	60	472
60	635	60	732	65	506
70	722	70	786	80	568
80	816	80	844	100	608

1) ($30\%\ Li_2WO_4 + 70\%\ Li_2SO_4$) – ($30\%\ K_2WO_4$ $70\%\ K_2SO_4$)• branches β-Li_2WO_4, D_2, K_2SO_4 intersect at 505° and 22% P_8; 625° and 59% P_8.

2) ($30\%\ Li_2WO_4 + 70\%\ Li_2SO_4$) – Li_2Cl_2, branches P_7 and Li_2Cl_2 intersect at 450° and 56.5% P_7. Branch Li_2Cl_2 is complicated by homeomorphic transformation at 565° and 85% Li_2Cl_2.

3) ($30\%\ K_2WO_4 + 70\%\ K_2SO_4$) – K_2Cl_2, branches P_8 and K_2Cl_2 intersect at 646° and 46.5% P_8.

4) Li_2Cl_2–K_2Cl_2 – eutectic at 348° and 42% K_2Cl_2.

• For convenience we will designate the composition ($30\%\ Li_2WO_4 + 70\%\ Li_2SO_4$) by P_7 and the composition ($30\%\ K_2WO_4 + 70\%\ K_2SO_4$) by P_8.

Diagonal Sections (Table 8, Figure 9)

1) $P_8-Li_2Cl_2$, – 2) branches Li_2Cl_2, β-Li_2WO_4, K_2Cl_2, K_2SO_4 intersect at 403° and 21.5% P_8, 470° and 35% P_8, 580° and 75% P_8. On branch Li_2Cl_2 homeomorphism was observed at 565° and 5% P_8. $P_7-K_2Cl_2$ – intersection of branches Li_2WO_4, K_2Cl_2 and D_2 at 475° and 27.5% K_2Cl_2; 475° and 32% K_2Cl_2.

Internal section: (50% P_8 + 50% P_7)$-K_2Cl_2$ (Table 8, Fig. 9).

TABLE 8

Diagonal				Section	
$P_8-Li_2Cl_2$		$P_7-K_2Cl_2$		50% P_8 + 50% P_7 $-K_2Cl_2$	
% P_8	Temperature	% K_2Cl_2	Temperature	% K_2Cl_2	Temperature
0	606°	0	608°	0	625°
5	565	10	544	10	578
15	472	20	500	15	557
20	418	25	485	17.5	548
30	450	27.5	475	20	542
35	470	30	478	22.5	548
40	518	32.5	480	25	555
50	576	37.5	475	30	565
60	585	40	500	40	590
70	585	50	576	50	614
75	580	60	612	60	640
80	660	70	656	70	668
–	–	80	696	–	–

TABLE 9

Point	Temperature	Composition (in mole%)				Equilibrium phases
		K_2Cl_2	P_7	P_8	Li_2Cl_2	
M_1	535°	15	40	45	–	K_2SO_4, D_2, K_2Cl_2.
M_2	460	–	32.5	32.5	35	Li_2WO_4, D_2, K_2Cl_2.
M_3	336	36.5	3.5	–	60	Li_2Cl_2, Li_2WO_4, K_2Cl_2.

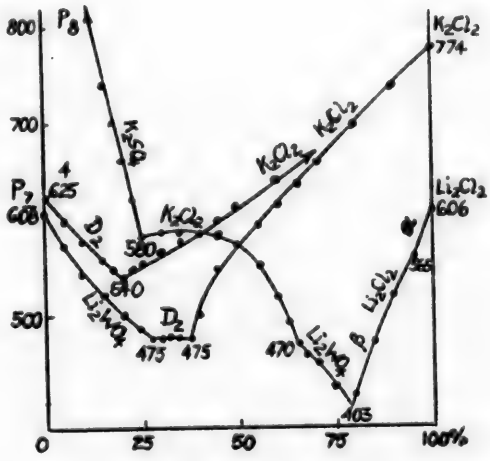

Fig. 9. Curves of Section III.

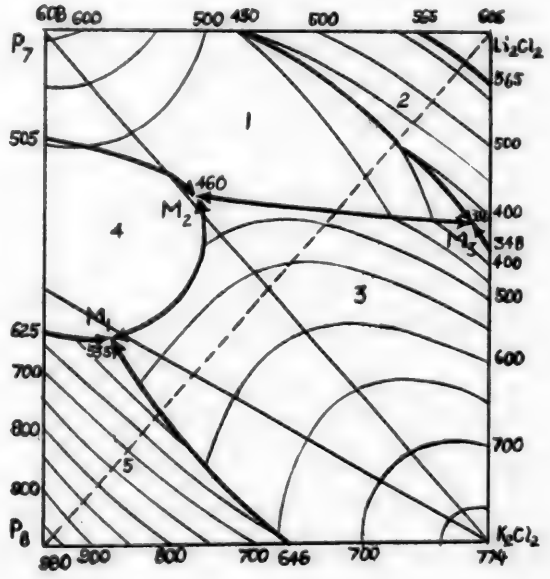

Fig. 10. Section III.
1) Li_2WO_4, 2) Li_2Cl_2, 3) K_2Cl_2, 4) $Li_2SO_4 \cdot K_2SO_4$, 5) K_2SO_4.

The branches of compounds $Li_2SO_4 \cdot K_2SO_4$ and K_2Cl_2 intersect at 540° and 19% K_2Cl_2.

As the result of studying the surface of crystallization of the given book section (Fig. 10) with the aid of ten cuts it was established that the five crystallization fields of the section converge into three univariant points. We present their compositions and temperatures in Table 9.

The areas of the crystallization fields in per cent of the total area of the rectangle are: K_2SO_4—12.70, field of compound $Li_2SO_4 \cdot K_2SO_4$—11.20, K_2Cl_2—44.28, Li_2WO_4—21.80, α - and β -Li_2Cl_2—10.02.

Characteristic for the field of compound $Li_2SO_4 \cdot K_2SO_4$ are its planar form and the absence of isotherms.

Melting without decomposition, the field retains its stability and takes up a large volume in the total volume of the prism, driving out to a considerable degree the fields of the components. The character of the isotherms in the fields of the starting components remains the same as in the previous book sections. The reaction of the system is toward complex formation.

The Three Book Sections of the Quaternary Reciprocal System Li, K ‖ Cl, SO_4, WO_4

It can be concluded, based on analysis of the data obtained as the results of their composition prism sectioning, that the presenee of eight crystallization volumes in the prism is supported by the three book sections, and their boundaries established.* The complex $Li_2SO_4 \cdot K_2SO_4$, obtained in the ternary reciprocal system Li, K ‖Cl, SO_4, appearing as the outer boundar y of the composition prism, is also confirmed inside the prism by book sections I and III.

In all three sections the reaction of complex formation predominates over the decomposition reactions.

As a result, the compound $Li_2SO_4 \cdot K_2SO_4$, melting without decomposition, retains its stability also inside the composition prism. It takes up quite a large volume in the prism, deeply penetrating into it and somewhat "oppressing" as it were the volume of the other complex $Li_2WO_4 \cdot K_2WO_4$, situated on the opposite side. This second complex, 1:1 $Li_2WO_4 \cdot K_2WO_4$, obtained in the ternary reciprocal system Li, K ‖ Cl, WO_4, is confirmed by book section II. The reaction of complex formation in this section predominates over the decomposition reactions to a considerably lesser degree than in the previous two book sections. This is also confirmed by the much smaller volume occupied by the tungstate complex 1:1 $Li_2WO_4 \cdot K_2WO_4$, when compared with the volume of the sulfate complex 1:1 $Li_2SO_4 \cdot K_2SO_4$.

SUMMARY

1. The three book sections through the reciprocal prism system Li, K ‖ SO_4, WO_4; were studied; namely P_3—P_4, P_5—P_6 and P_7—P_8. As a result of this study the volumes of the two complexes $Li_2SO_4 \cdot K_2SO_4$ and $Li_2WO_4 \cdot K_2WO_4$.

2. Six sections through the upper and lower bases of the prism were studied and it was established that they appear as the sections of two branches with points of intersection at: P_3—Li_2Cl_2 with univariant point 460° and 52.5% P_3; P_4—K_2Cl_2—620° and 50% K_2Cl_2, P_5—Li_2Cl_2—475° and 46.5% P_5; P_6—K_2Cl_2—600° and 45% K_2Cl_2; P_7—Li_2Cl_2—450° and 56.5% P_7; P_8—K_2Cl_2—646° and 46.5% P_8.

3. The liquidus diagrams of the three book sections P_3—P_4—Li_2Cl_2—K_2Cl_2, P_5—P_6—K_2Cl_2—Li_2Cl_2, P_7—P_8—K_2Cl_2—Li_2Cl_2.

4. As a result of our study the presence of eight crystallization volumes in the prism was established, of which two belong to the complexes $Li_2SO_4 \cdot K_2SO_4$ and $Li_2WO_4 \cdot K_2WO_4$ and six are volumes of the starting components K_2Cl_2, K_2SO_4, K_2WO_4, Li_2Cl_2 (α and β), Li_2WO_4 (α and β), Li_2SO_4.

5. The complex $Li_2SO_4 \cdot K_2SO_4$ takes up a large volume in the prism, being deeply diffused in it. The complex $Li_2WO_4 \cdot K_2WO_4$ takes up a much smaller volume. The form of both complexes is planar.

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Received February 17, 1954.

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THERMOGRAPHIC STUDY OF THE DECOMPOSITION OF BIVALENT METAL OXALATES

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There is hardly any literature data on the thermal decomposition of metal oxalates, and the available data on individual salts is incomplete and frequently contradictory. In addition, the process of dehydration (in the case of crystallohydrates) is frequently confused with the thermal decomposition of the oxalate itself.

Despite this, the decomposition of oxalates, expecially of the heavy metals, is of interest not only from the theoretical viewpoint but also from the practical side, having in mind the preparation of solid phases in chemically active form (metals, oxides, etc.).

With the aid of the thermographic method we studied the decomposition of the oxalates of Fe, Ni, Co, Mn, Cu, Zn, Cd, Hg, Sn, Pb, Mg, Ca, Sr, Ba, and also of oxalic acid. The oxalates were precipitated from the solutions of soluble metal salts (previously purified) with pure alkali oxalates (or oxalic acid) and dried at 80-100°.

In the precipitation of the oxalates care was taken not to add the alkali oxalates in amounts exceeding the theoretical so as to avoid the formation of double salts of the type $M_2C_2O_4 \cdot 3C_2O_4$, possessing entirely different solubility properties. Thus, the double oxalates of Ni and Co are difficultly soluble, while the corresponding iron derivative is readily soluble.

EXPERIMENTAL

The thermograms were made on the recording instrument of the N. S. Kurnakov system, in which programmatic thermal regulation was realized with the aid of a sensitive thermal control element and Thyratron relay, assembled according to the phase rotation scheme [1]. The potentiometric method [2] was used to calibrate the Pt-PtRh thermocouple. Al_2O_3 was used as the standard.

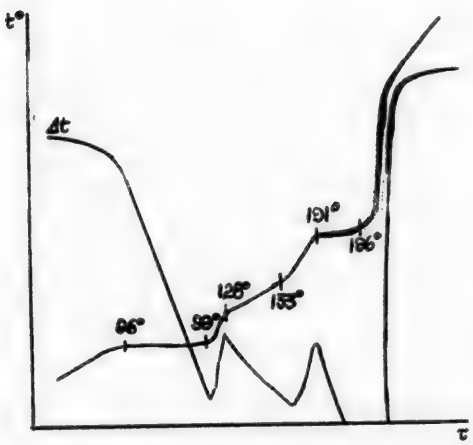

Fig. 1. Thermogram of oxalic acid, dihydrate.

According to Karyakin [3], the dihydrate of oxalic acid loses water at 98-99°, while anhydrous $H_2C_2O_4$ obtained by distillation (vacuum) melts at 189° and decomposes above this temperature into CO, CO_2, H_2O. Our thermogram for crystalline $H_2C_2O_4 \cdot 2H_2O$, obtained by the method of Kolthoff and Sandell [4], is shown in Fig. 1. As can be seen from the thermogram, water is removed at 96-99°, the acid melts at 128-153° and decomposes at 191-196°. $H_2C_2O_4$ is amorphous after removal of the water of crystallization, and consequently is characterized by a melting point range [5]. As a result, the softening of amorphous $H_2C_2O_4$, unsuccessful in attaining the crystalline state with the liberation of stored internal energy, differs from the melting of the crystalline acid $H_2C_2O_4$, obtained by distillation in vacuum (m.p. 189°).

As regards the oxalates of the bivalent metals, from the character of their thermal decomposition they can be divided into two groups. The oxalates of copper and mercury, decomposing with the evolution of heat, belong to the first group. In the thermogram for copper oxalate (Fig. 1) the weakly expressed endothermic effect denotes the removal of water, while the exothermic peaks of the ordinary and differential graphs characterize the decomposition of the anhydrous salt. In order to prove that the exotherm 320-376° relates specifically to the thermal dissociation of the oxalate, and not to the transition of CuC_2O_4 from the amorphous state (after water removal) into the crystalline state, we performed

a visual experiment in the Stapanova vessel. On doing this, the pale blue CuC_2O_4 (after the endotherm) at the moment of sharp galvanometer needle deflection in the direction of heat evolution begins to rapidly turn into a dark brown mass, which is shown to be a mixture of metallic copper and its oxides.*

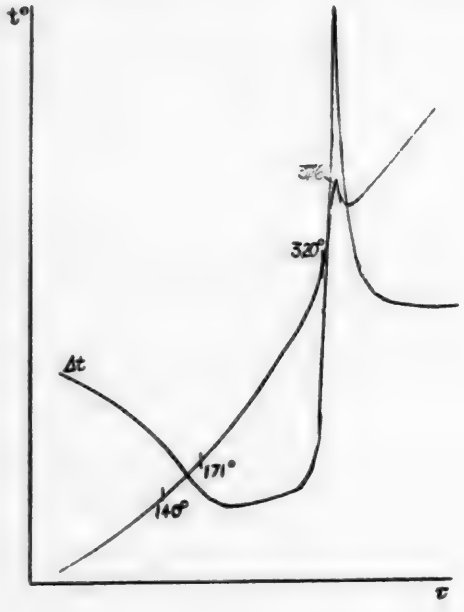

Fig. 2. Thermogram of copper oxalate

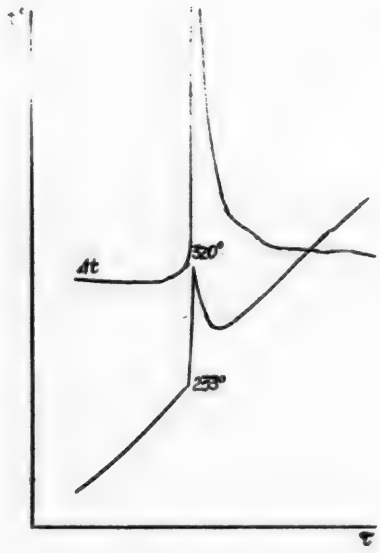

Fig. 3. Thermogram of mercury oxalate.

The endotherm is absent in the thermogram for the decomposition of HgC_2O_4 (Fig. 3) inasmuch as mercury oxalate cyrstallizes without water, while the exotherm is even more strongly expressed than in the case of copper oxalate. The specimen suffers a spontaneous rise in temperature of about 90° (exotherm 233-320°). According to Nikolaev [6], similar peaks on ordinary graphs characterize autocatalytic reactions, i.e., their rate increase is proportional to the time. Consequently, there is basis to assume that the thermal decomposition reactions for copper and mercury oxalates are autocatalytic reactions.

The oxalates of the remaining metals studied by us belong to the second group, the thermal dissociation of which is accompanied by the absorption of heat. The thermograms for $FeC_2O_4 \cdot 2H_2O$, $NiC_2O_4 \cdot 2H_2O$, $CoC_2O_4 \cdot 2H_2O$, $MnC_2O_4 \cdot 2H_2O$, $ZnC_2O_4 \cdot 2H_2O$, $MgC_2O_4 \cdot 2H_2O$, $CdC_2O_4 \cdot 3H_2O$ are essentially of one type and invididually possess two endothermic effects for the removal of water and decomposition of the anhydrous salt. As an example of a typical thermogram we will present the heating curve for $MnC_2O_4 \cdot 2H_2O$ (Fig. 4). Here the first endotherm 93-125° characterizes dehydration, while the second (384-412°) characterizes the decomposition of anhydrous manganese oxalate. The oxalates of the metals Co, Zn and Cd give thermograms that are of similar character but, it is understood, with different temperature values for the endothermic effects (see Table). The heating curve for $NiC_2O_4 \cdot 2H_2O$ (Fig. 5) differs somewhat from the typical thermogram in that after the removal of water, the differential graph does not return to the level of the null line (for the differential thermocouple) and the decomposition of NiC_2O_4 begins immediately, as a result of which both of the endothermic effects are not as clearly expressed as in the typical thermogram. This is explained by the greater strength of the water bond in $NiC_2O_4 \cdot 2H_2O$ (dehydration temperature is higher; see Table), after the removal of which the salt itself decomposes with comparative ease.

A peculiarity of the thermogram for $FeC_2O_4 \cdot 2H_2O$ (Fig. 6) is the presence of superheat curves [7] with respect to dehydration (214-200°). The superheat cycle shows that after the begining of dehydration (214°) the temperature drops appreciably (200°), i.e., $FeC_2O_4 \cdot 2H_2O$ is superheated by 14°. An even greater superheat cycle at the same heating rate of 12° a minute characterizes the heating curve for anhydrous PbC_2O_4 (Fig. 7), where after the beginning of salt decomposition (354°) the temperature drops to 318°. Such marked superheating (by 36°) is seen only in the case of old samples of PbC_2O_4. The curve for freshly prepared PbC_2O_4 is shown in Fig. 8**, where the superheat cycle is

* The decomposition of copper oxalate proceeds according to the equation $CuC_2O_4 = Cu + 2CO_2$. The copper that separates is partially oxidized. ** Freshly precipitated PbC_2O_4 was separated and dried at 110° for one hour.

expressed much more weakly (by 15°) than on the curve for an old sample of PbC_2O_4 (Fig. 7). In addition, in Fig. 8 an exothermic peak can clearly be seen for not only the differential, but also for the ordinary graph, which speaks of the conversion of the unstable amorphous PbC_2O_4 into the stable crystalline form with the evolution of excess internal energy.

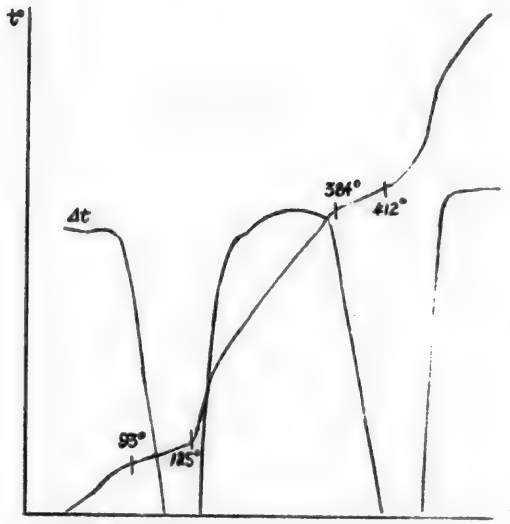

Fig. 4. Thermogram of manganese oxalate.

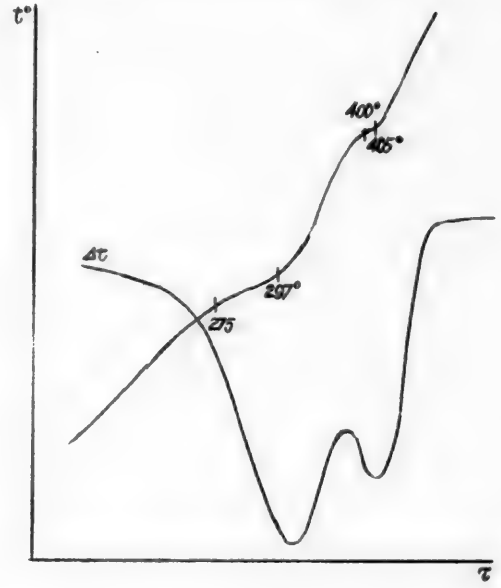

Fig. 5. Thermogram of nickel oxalate.

TABLE

Substance	Temperature interval		Solid decomposition products
	Removal of water	Decomposition of oxalate	
$H_2C_2O_4 \cdot 2H_2O$	96–99°	191–196°	–
$NiC_2O_4 \cdot 2H_2O$	275–295	400–405	Ni
$CoC_2O_4 \cdot 2H_2O$	219–233	400–409	Co
$FeC_2O_4 \cdot 2H_2O$	214–200*	371–379	Fe
$MnC_2O_4 \cdot 2H_2O$	93–125	384–412	MnO
$ZnC_2O_4 \cdot 2H_2O$	188–230	414–426	ZnO
$MgC_2O_4 \cdot 2H_2O$	196–212	421–419*	MgO
$CdC_2O_4 \cdot 3H_2O$	106–118	368–398	Cd + CdO
PbC_2O_4	–	354–318*	PbO
SnC_2O_4	–	350–342*	SnO_2
$CaC_2O_4 \cdot H_2O$	105–110	263–285	$CaCO_3$
$SrC_2O_4 \cdot H_2O$	122–164	182–194	$SrCO_3$
BaC_2O_4	–	226–246	$BaCO_3$
HgC_2O_4	–	233–320	Hg + HgO
$CuC_2O_4 \cdot 2H_2O$	140–171	320–376	Cu + CuO

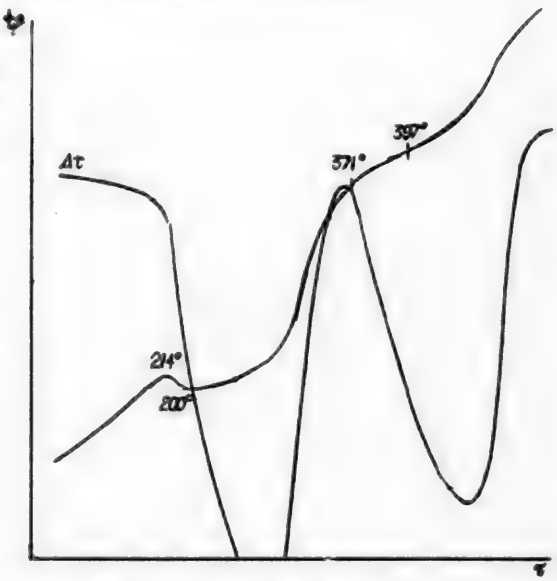

Fig. 6. Thermogram of iron oxalate.

Similar transitions from the unstable to the stable state of the solid are also observed in other thermograms. Thus, for example, in the case of the heating curve for SnC_2O_4 (Fig. 9), in addition to the superheat cycle, we have an exothermic effect (541-566°) for the transition of the liberated tin dioxide from the amorphous into the crystalline state. It is self-understood that this process is thermodynamically irreversible, consequently the graph of the heating curve for very slowly cooled SnO_2, obtained from the decomposition of SnC_2O_4, fails to show an exothermic effect in the thermogram.

* Presence of superheating.

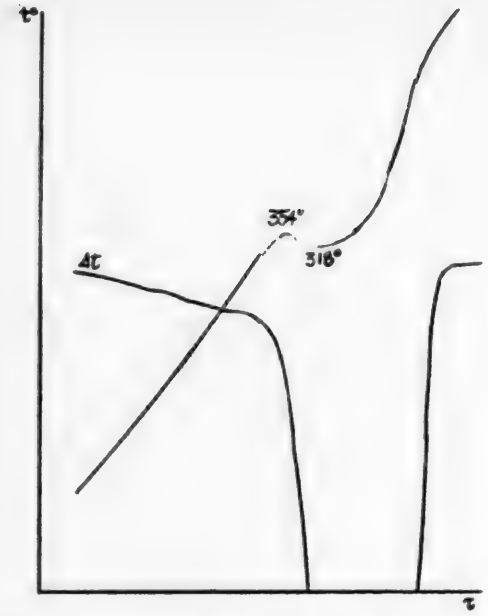

Fig. 7. Thermogram of an old specimen of lead oxalate.

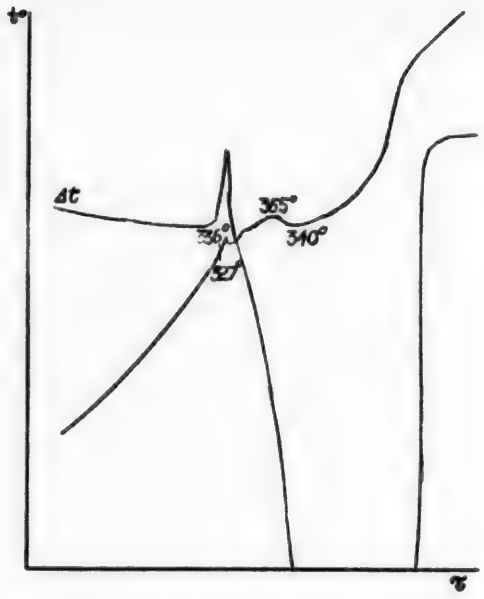

Fig. 8. Thermogram of freshly precipitated lead oxalate.

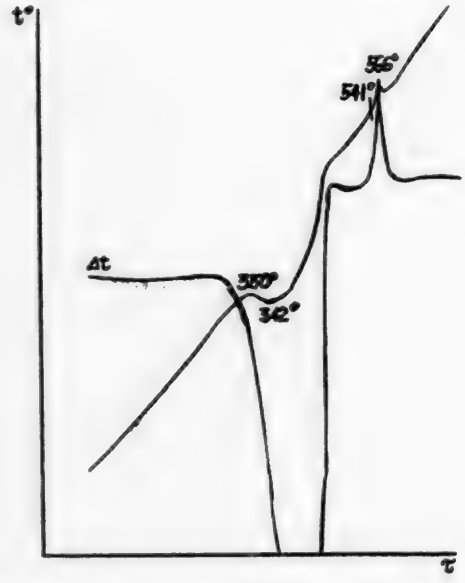

Fig. 9. Thermogram of stannous oxalate.

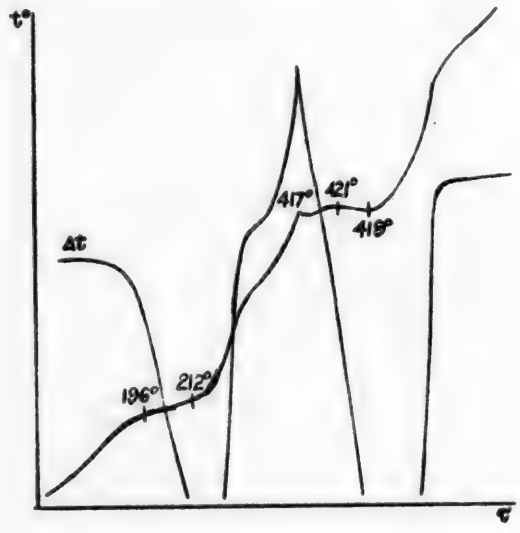

Fig. 10. Thermogram of magnesium oxalate.

In the decomposition of magnesium oxalate we have an interesting example of unstable solid formation. In the thermogram of $MgC_2O_4 \cdot 2H_2O$ the exothermic peak for the transition from unstable anhydrous salt into the stable (crystalline) form is fixed between two endotherms, after which the thermal decomposition of MgC_2O_4 takes place (Fig. 10). In the other thermograms (Fig. 4, 5, 7, 8, 11) the amorphous stage cannot be detected, probably for the reason that the transition (crystallization) rate is greater than the thermal decomposition rate [8].

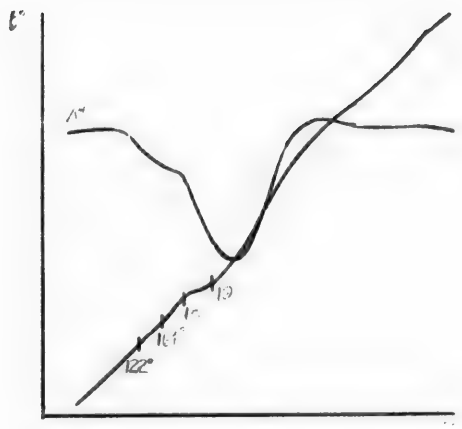

Fig. 11. Thermogram of strontium oxalate.

The oxalates of the alkaline earth metals, suffering thermal dissociation into carbon monoxide and the metal carbonates, also give singular type thermograms.

The heating curve for strontium oxalate is shown in Fig. 11, where the dehydration process is weakly depicted while a distinct endothermic effect characterizes the decomposition of SrC_2O_4. When compared with the thermograms for the oxalates of the transition elements tin, lead and magnesium, the thermal decomposition endotherms for the oxalates of the alkaline earth elements are incomparably more weakly defined on the heating curves (under the same thermographing conditions). Apparently, the more profound decomposition of the oxalates of Fe, Co, Ni, Mn, Zn, Cd, Sn, Pb and Mg to the free metals and metal oxides (see Table) is associated with the absorption of a large amount of heat when compared to the decomposition of CaC_2O_4, SrC_2O_4 and BaC_2O_4 with the formation of carbonates.

In conclusion, we present the numerical data for the thermal dissociation of the oxalates studied by us, the reproducibility of which was demonstrated by the method of comparing several thermograms of different specimens of the same salt (see Table).

SUMMARY

1. The thermographic method was used to characterize the oxalates of the bivalent metals Ni, Co, Fe, Mn, Zn, Cd, Mg, Pb, Sn, Ca, Sr, Ba, Hg, Cu and the dihydrate of oxalic acid.

2. The endothermic and exothermic type of heating curves for the thermal decomposition of bivalent metal oxalates was established.

3. It was observed that the decomposition of copper and mercury oxalates is autocatalytic in nature.

4. It was shown that superheating is present in both the dehydration process and during the decomposition of the anhydrous salts. The oxalates without water of crystallization (SnC_2O_4, PbC_2O_4), give a well defined superheat cycle.

5. The irreversible transformation of the unstable form of a solid into the thermodynamically stable crystalline state was observed in a number of cases.

6. The form of the thermograms depends on the character of oxalate decomposition. In connection with this the thermogram for the decomposition of magnesium oxalate ($MgC_2O_4 \rightarrow MgO$) differs sharply from the thermograms for the oxalates of the alkaline earth metals ($MC_2O_4 \rightarrow MCO_3$).

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Received February 22, 1954.

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EXCHANGE OF RADICALS BETWEEN ORGANIC COMPOUNDS IN SOLUTION

I. P. Gragerov

The mobility of radicals in organic compounds determines to a large degree their chemical behavior. The ease of their exchange reactions can serve as a measure of radical mobility, whence such reactions of similar radicals, the study of which is possible only by means of the isotopic method, give the rules for mobility in the least distorted form. In contrast to the large number of studies made on the exchange of hydrogen isotopes, only a few studies have been made on the exchange of similar alkyl or aryl radicals between different organic molecules. Only three studies in this field are to be found in the literature [1].

In the present work we studied the exchange of methyl, ethyl and phenyl residues between two compounds in solution. Deuterium was substituted in one of the components of the radical exchange reaction.

A summary of the exchange experiments is given in the Table. From the presented data it can be seen that heavy ethyl bromide fails to exchange its ethyl radicals with either phenetole or ethyl acetate, even under drastic conditions. The same is true with respect to the exchange of phenyl groups between heavy iodobenzene and anisole.

A considerable degree of exchange even under the mildest conditions is observed between ethyl bromide and ethyl iodide, but not between the latter and phenetole. Ethyl bromide exchanges even more easily with diethyl sulfate.

Heavy dimethyl sulfate readily exchanges the methyl radicals with methyl iodide and methyl acetate, but not with the methyl ester of p-toluenesulfonic acid. On the other hand, the latter compound quite readily exchanges with methyl iodide. Exchange between methyl iodide and anisole is not observed under these conditions.

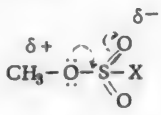
In the presence of acetic acid there is an exchange of radicals between ethyl bromide and ethyl acetate. The exchange between these two compounds proceeds in nitrobenzene medium, which apparently is explained by the presence of acetic acid formed as a result of decomposition of the reaction mixture. (Acetic acid was isolated by us in these experiments).

The presence of anhydrous aluminum bromide fails to lead to exchange between phenetole and ethyl bromide. The loss of deuterium by heavy ethyl bromide in these experiments is associated with its dilution by the light compound, formed in accord with the equation [2].

$$C_6H_5OC_2H_5 + AlBr_3 \rightarrow C_6H_5OAlBr_2 + C_2H_5Br.$$

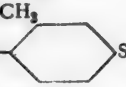
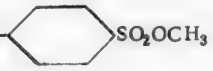
An explanation of all of the above given data from one viewpoint presents certain difficulties. The most probable is the postulation that the exchange proceeds through the intermediate formation of onium compounds. The ease of formation of onium compounds, which also means the ease of exchange, should be determined by the properties of both components of the exchange reaction – the ability of one of them (acceptor) to add the positively charged residues and the ability of the second (donor) to give them away. The acceptor properties depend on the degree of freedom possessed by the electron pairs of the onium atom former; the donor properties depend on the degree of polarity of the bond cleaving the positively charged residue.

Proceeding from these considerations, it becomes possible to satisfactorily explain our results in the following manner: dimethyl sulfate and the methyl ester of p-toluenesulfonic acid are poor acceptors, inasmuch as the SO_2 group draws the electrons away from oxygen.



This structural characteristic makes them excellent donors. Absence of methyl group exchange between these compounds is due to the fact that they cannot form an oxonium compound with each other. Rather, they should readily undergo exchange with good acceptors, i.e., according to the scheme:

Conditions and Results of the Exchange Experiments

Exchanging Compounds	Temperature	Time (in hours)	Excess density of the water from the combustion (γ)				Per cent of exchange*
			of the starting heavy compound	calculated for the exchange radicals of both components in the equilibrium reaction	Found		
					in the heavy component	in the exchange radical of the light component	
4.5 g C_2D_5Br and 4.9 g $C_6H_5OC_2H_5$	193*	40	1817	900	1770	8	–
4.3 g C_2D_5Br and 4.6 g $CH_3COOC_2H_5$	193	40	1817	780	1770	30	–
3.7 g C_2D_5Br and 5.9 g C_2H_5I	193	9	1817	860	1544	226	26
2.5 g C_2D_5Br and 3.1 g $(C_2H_5)_2SO_4$	153	10	973	335	–	206	58
4.6 g C_2D_5Br and 4.4 g $CH_3COOC_2H_5$ with 12 g $C_6H_5NO_2$	193	40	1817	830	–	270	33
3.8 g C_2D_5Br and 4.4 g $CH_3COOC_2H_5$ with 10 g $C_6H_5NO_2$	198	37	1817	750	–	330	44
2.1 g C_2D_5Br, 3.2 g $CH_3COOC_2H_5$ and 0.6 g CH_3COOH	194	40	973	340	–	210	62
5 g C_2D_5Br, 6.5 g $C_6H_5OC_2H_5$ and 3.4 $AlBr_3$	20	2	1817	845	1747	20	–
3 g C_2D_5Br, 5.2 g $C_6H_5OC_2H_5$ and 4.4 g $AlBr_3$	62	22	973	375	580	24	–
3.7 g C_2D_5I and 4 g $C_6H_5OC_2H_5$	156	29	1118	480	1138	6	–
4.6 g CD_3I and 6.1 g $C_6H_5OCH_3$	156	29	1593	578	–	6	–
10.2 g C_6D_5I and 5.9 g $C_6H_5OCH_3$	180 200	15 4	1480	881	1400	26	–
2 g $(CD_3)_2SO_4$ and 5.2 g CH_3I	150	6	546	250	292	215	86
2 g $(CD_3)_2SO_4$ and 2 g CH_3COOCH_3	154	6	546	290	270	270	93
2.3 g $(CD_3)_2SO_4$ and 2.6 g CH_3COOCH_3	125	7.5	672	342	507	202	59
2 g $(CD_3)_2SO_4$ and 2.5 g CH_3COOCH_3	99	10	672	317	654	58	18?
2 g $(CD_3)_2SO_4$ and 2 g CH_3COOCH_3	61	4	546	288	522	24	–
2.3 g $(CD_3)_2SO_4$ and 3.4 g 	99	13	672	474	715	35	–
3 g $(CD_3)_2SO_4$ and 4.5 g	126	8	672	452	703	47	–
2.4 $(CD_3)_2SO_4$ and 4.2 g 	156	6	672	419	666	23	–
3.3 g $(CD_3)_2SO_4$ and 3.9 g	156	10	687	488	639	57	12?
3.8 g CD_3I and 4 g	156	10	1593	689	1290	270	39

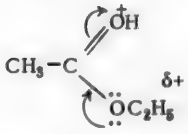
* Based on the amount of deuterium in the light component of the exchange reaction.

$$\left(X = -OCH_3 \text{ or } \text{C}_6\text{H}_4\text{-}CH_3\right),$$

which scheme also explains the exchange with methyl iodide and methyl acetate.

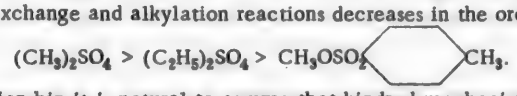
Ethyl bromide fails to exchange with phenetole and ethyl acetate because of insufficient polarity. For the same reason there is no exchange between methyl iodide, ethyl iodide and iodobenzene, on the one hand, and anisole and phenetole on the other. In the exchange with diethyl sulfate the ethyl bromide apparently functions as the acceptor, and the reaction proceeds in accord with an analogous scheme [1]•

The catalytic influence of acetic acid on the exchange between ethyl bromide and ethyl acetate can be explained by the increase in the donor ability of one of the components in the reaction, probably the ethyl acetate, under the influence of the added proton (see scheme).



The absence of exchange between ethyl bromide and phenetole in the presence of aluminum bromide is probably explained by the fact that all of the aluminum bromide is combined with the phenetole in a stable complex, and consequently the compound $C_2H_5-AlBr_4$, cannot be formed, which, if it were present in the mixture, should readily exchange its ethyl groups with phenetole.

The unquestionable bond existing between the ease of radical exchange and the alkylation tendency should be mentioned: the ease of the exchange and alkylation reactions decreases in the order



On the basis of this relationship it is natural to assume that kindred mechanisms prevail for both types of reactions, and to consider the donor properties of the alkylating agent and the acceptor properties of the substance being alkylated as playing an important role also in alkylation reactions.

EXPERIMENTAL

Heavy ethyl bromide was obtained by the addition of heavy hydrogen bromide to ethylene, using the method proposed by Gustavson [3], under the conditions worked out for light substances [4]. Into a solution of 11 g of anhydrous aluminum bromide in 6.5 g of ethyl bromide, cooled to −78° with a mixture of solid carbon dioxide and acetone, was rapidly passed a dry mixture of heavy hydrogen bromide and ethylene, cooled down to the same temperature (the ethylene was taken in slight excess).

Hydrogen bromide was obtained from dilute heavy water, red phosphorus and bromine. The usual method was changed for the sake of water economy: for 17.4 g of phosphorus was taken 28.5 g of water and 180 g of bromine. The hydrogen bromide was purified from bromine in a tube filled with broken glass and a mixture of 1 g of red phosphorus with 1 g of heavy water. The reaction mass and purification system at the end of the operation were heated with a burner. The gas was dried over calcium chloride that had been heated at 400°, and prior to entering the reaction vessel it was passed through a gas meter containing nitrobenzene.

The crude ethyl bromide was treated with ice, washed with soda water, again with water and then dried over calcium chloride. The yield was 63% of the theoretical, based on water taken. Fractional distillation gave the pure substance, b.p. 38.0-38.5° at 764 mm and d_4^{20} 1.4586.

Heavy ethyl iodide was prepared by the reaction worked out for light substances [5]. The mixture of equivalent amounts of heavy ethyl bromide and methyl iodide was heated for several hours with a small amount of anhydrous aluminum chloride. The addition of fresh $AlCl_3$ was made 3-4 times during the heating period. The reaction mixture was treated with water, the lower layer was separated, washed with alkali, water, dried and distilled. The obtained ethyl iodide had b.p. 69.5-72° at 739 mm and d_4^{20} 1.9393.

Heavy iodobenzene was obtained by the usual method from aniline containing deuterium in the ortho- and

• Proceeding from the developed considerations, the exchange between ethyl bromide and ethyl iodide is explained with difficulty. It is quite possible that the exchange depends on the dissociation of the iodide into the $C_2H_5^{\cdot}$ radical and atomic iodine.

para- positions of the ring. The latter was prepared by heating ordinary aniline with heavy water and a small amount of sulfuric acid at 150° for 6 hours [6].

Heavy dimethyl sulfate was prepared by us for the first time. The synthesis sequence is as follows:

$$CH_3NO_2 \xrightarrow{D_2O} CD_3NO_2 \xrightarrow[HCl]{Fe} CD_3NH_2 \cdot HCl \xrightarrow{AgNO_2} CD_3OH \xrightarrow{\text{oleum}} (CD_3)_2SO_4.$$

50 g of nitromethane was heated in an ampoule for 12 hours at 98° with 1.4 g of D_2O (99.6%), 1 g of anhydrous sodium acetate, and 1 g of glacial acetic acid [7]. The water layer was then separated, and the nitromethane without purification was used for reduction. The amount of deuterium in the combustion water from nitromethane was 6200 γ (instead of calculated 5700 γ).

The nitromethane was reduced by the method [8] already used for the preparation of heavy methylamine [9]. To 50 g of nitromethane was added 120 ml of boiled water and 170 g of iron turnings. The air from the apparatus was displaced with hydrogen and in a stream of hydrogen, with mixing, there was added 110 ml of concentrated hydrochloric acid at such a rate that the temperature failed to rise above 70° and the reaction mass remained acid all of the time. The reaction mass (having lost the odor of nitromethane) was then made alkaline with 100 g of KOH, and the methylamine was steam distilled (about 1 liter of distillate) into a receiver containing 20% HCl solution. The obtained solution of methylamine hydrochloride was evaporated to dryness on the water bath. The yield was 45 g. The amount of deuterium in the combustion water was 3980 γ. The loss of a considerable portion of the deuterium is explained by the reaction of nitromethane with hydrochloric acid and water during reduction.

Heavy methylamine was converted into heavy methyl alcohol by the method developed for light substances [10]. With ice cooling 44 g of heavy methylamine hydrochloride was ground with 111 g of silver nitrate and 30 ml of water. The liquid was suction filtered and the residue was extracted five times with water. The water extract was acidified with 5% sulfuric acid and boiled in a flask under reflux. When the evolution of nitrogen slackened, new portions of acid were added. The boiling was continued until gas evolution ceased.* The reaction mass was then distilled from a flask fitted with a long column. The fraction, distilling at 96-99.5° at 753 mm, in amount 200 ml, was saturated with potash and distilled. The single repetition of such a fractional distillation gave 7.2 g of methyl alcohol. The yield was 34% of the theoretical (b.p. 65-67°). As was shown by analysis, there was no loss of deuterium in this stage.

Heavy dimethyl sulfate was prepared from heavy methyl alcohol by the method developed for light substances [11]. To 17.6 of methyl alcohol with ice cooling there was gradually added, with shaking, 79 g of 60% oleum, and the reaction mixture was distilled in vacuum. A second fractional distillation in vacuum gave 23.4 g of pure dimethyl sulfate, which after shaking with MgO to alkaline reaction, distilled at 104-104.5° at 46 mm, d_4^{20} 1.3257. The yield was 66% of the theoretical. There was no loss of deuterium in this stage also.

Heavy methyl iodide. Modifications were introduced into the usual method for the preparation of this substance in the interest of maximum utilization of the heavy alcohol: for 7.3 g of alcohol there was taken 3 g of red phosphorus and 33 g of iodine, which permitted increasing the yield of CD_3I up to 25 g (77%). The constants of the substance, used in the experiments, were as follows: b.p. 41-41.5° at 744 mm, d_4^{20} 2.276.

Exchange experiments. The weighed mixture of heavy and light substances was sealed in a glass ampoule and heated for a definite period of time at the given temperature. In some of the experiments, in addition to the components undergoing exchange, the ampoule contained nitrobenzene, acetic acid, or aluminum bromide. The contents of the ampoule were separated into components by fractional distillation. In the experiments with dimethyl sulfate, diethyl sulfate, methyl ester of p-toluenesulfonic acid, and in part of the experiments with anisole and phenetole the fractional distillation was performed in vacuum. In the experiments with aluminum bromide the reaction mixture was treated with ice, the separated lower layer was washed with water, 10% alkali, again with water and then dried prior to distillation.

With the aid of the density determination method we assured ourselves as to sufficient purity of the isolated substances, the density values for which revealed that the presence of other components of the exchange reaction did not exceed 0.5-2%.

The substances isolated in the above described manner were burned over copper oxide and the obtained combustion waters, after adding a small amount of alkali, were analyzed for deuterium content by the microflotation method

* The evolved gas, in addition to nitrogen, contained methyl nitrite, which was removed by liquid air cooling. Heavy methyl alcohol was obtained from this product by heating it in a sealed tube with KOH solution.

with an accuracy to 3%.

A comparison of Column 4 with Columns 6 and 7 in the Table reveals that a satisfactory deuterium balance was obtained in all of the experiments, which fact supports the validity of the analyses.

I am indebted to A. I. Brodsky for his assistance in the work.

SUMMARY

1. The isotopic method was used for studying the exchange of similar ethyl, methyl and phenyl radicals between a number of organic compounds with heating of their mixtures, and also their mixtures with certain additives.

2. The obtained data are explained on the basis of postulating that the exchange proceeds through the intermediate formation of onium compounds.

3. A parallelism was found to exist in the ease of exchange reactions and of alkylation reactions, indicating their kindred mechanism.

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Received February 15, 1954

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PHYSICO-CHEMICAL ANALYSIS OF BINARY SYSTEMS FORMED BY UREA WITH PHENOLS. IV.

N. Z. Rudenko and D. E. Dionisyev

Along with other methods, the physico-chemical analysis method is currently finding use in solving the problems of mutual atomic influence in molecules. The use of this method makes it possible to establish the facts of chemical reactivity between components in those cases where other study methods prove to be powerless.

If in the study one component remains constant, while the second components differ from each other only by individual atoms, then as a first approximation the changes in the system can be regarded as being due to the influence of this atom on the organic molecule as a whole.

It was shown by us in earlier published papers that urea with phenol gives an unstable compound that is completely dissociated in the liquid phase [1]. A second hydroxyl group in the nucleus leads to the formation of a more stable urea compound with dihydric phenols but of different composition than the compound with phenol; the stability of these compounds changes with change in the position of the second hydroxyl group [2]. The molecular compounds of urea with hydroquinone and of urea with resorcinol, undergoing intramolecular reaction, give a new ternary compound [3].

In the present study we investigated the systems formed by urea on the one hand, and p-nitrophenol, o-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitriphenol on the other. These investigations were made for the purpose of elucidating the influence of the position and number of nitro groups in the phenol molecule on the character of reaction with urea.

The melting, density, viscosity, and electrical conductivity methods were used to study the system. The method was described earlier [1]; measurements in the liquid phase were made at three temperatures. The concentrations were always expressed in mole per cent, the viscosity in centipoises.

The hydroxyl hydrogen of phenol is probably the reactive site in the formation of urea compounds with the earlier investigated phenols. When nitro groups are present in the phenol nucleus it is possible to have compound formation as the result of these nitro groups.

To solve this problem we undertook a study of the systems that are formed when urea is reacted with nitrobenzene, p-nitrotoluene, and o-nitrotoluene. Separation in these systems was observed at all concentration ranges.

The system urea-p-nitrophenol was studied by the melting method by Kremann and Rodinis [4], who established the presence of a 1:1 compound. We repeated the melting study, and also investigated the density, viscosity, and electrical conductivity at 120, 130, and 140°.

After repeated recrystallization from water the urea used in the study had m.p. 132.7°. After two recrystallizations from alcohol the C.P. p-nitrophenol had m.p. 113.2°.

Our data on melting, given in Fig. 1, differ somewhat from the data of Kremann. The melting temperature of compound $CO(NH_2)_2 \cdot C_6H_5O_3N$ is 116.2°. The eutectic points at 70 and 20 mole % of urea have m.p. 110.7 and 91.5°, respectively.

The viscosity curves (Fig. 2) rise quite sharply from urea, pass through a maximum at 50-60 mole % urea, and descend to p-nitrophenol. With elevation of the temperature the maximum shifts toward the urea side. The temperature coefficient of the viscosity is also greatest in the region corresponding to 50 mole %.

The isotherms of the density are shown in Fig. 3, appearing as curves that are slightly convex to the composition axis.

The isotherms of the electrical conductivity (Fig. 4), slowly rising from the electrical conductivity of p-nitrophenol, begin to rise more rapidly at 70 mole % urea, and for the isotherms at 140° they pass through a maximum in the region of 90 mole % urea.

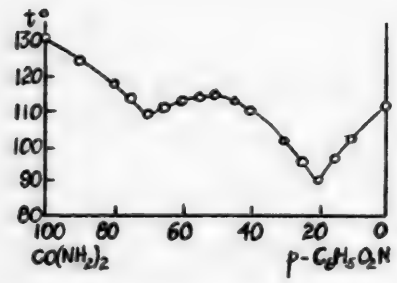

Fig. 1. Melting point curve of the system urea-p-nitrophenol.

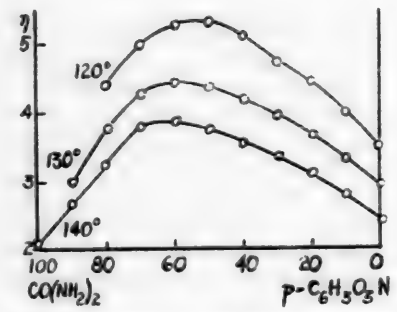

Fig. 2. Viscosity curves of the system urea-p-nitrophenol.

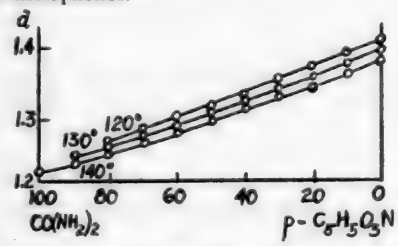

Fig. 3. Density curves of the system urea-p-nitrophenol.

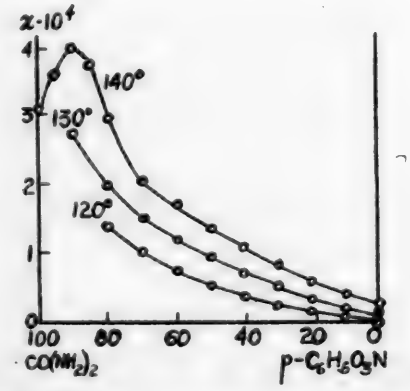

Fig. 4. Electrical conductivity curves of the system urea-p-nitrophenol.

Correcting the electrical conductivity for viscosity ($\eta\kappa$), as is to be expected, makes the isotherms somewhat straighter in the region of 70 mole % urea, but it fails to change the general course of the curve (Fig. 5). The maximum is found at 90 mole % urea and for the 140° isotherms it corresponds to $\eta\kappa = 10.88 \cdot 10^4$ (for urea $\eta\kappa = 6.42 \cdot 10^4$).

System urea-o-nitrophenol was studied by the melting method by Kremann and Rodinis [4]. The occurrence of stratification was established by them. Our attempts to study this system in the liquid phase proved unsuccessful, inasmuch as we were unable to get complete miscibility even with considerable increase in temperature.

System urea-2,4-dinitrophenol was studied by the melting method by Puschin and Rikowski [5]. They obtained a curve with a eutectic and made the conclusion that chemical interaction between the components is absent in the system. We repeated the melting study, and also investigated the viscosity, density, and electrical conductivity at 120, 130, and 140°.

Chemically pure dinitrophenol was taken for the study, which after recrystallization from benzene had m.p. 114.7°.

The melting point curve for the system is shown in Fig. 6. The curve consists of three branches – two branches showing the crystallization of the pure components and one branch showing the crystallization of the compound $2CO(NH_2)_2 \cdot C_6H_4O_5N_2$ with m.p. 116.4°. The eutectic points with m.p.112.5 and 95° respectively have the composition 80 and 40 mole % urea. The sharp difference from the melting curve obtained by Puschin and Rikowski is explained by the fact that in the region of the maximum exceedingly strong supercooling of the mixtures takes place, reaching a value of 20-30°. Only as the result of vigorous stirring and seeding were we able to produce a maximum on the curve, which at first escaped us also.

The viscosity isotherms (Fig. 7) have a maximum in the region of 75 mole % urea, which with elevation of the temperature shifts slightly toward the urea side (up to 78 mole %). The convexity of the isotherms to the composition axis in the region rich in dinitrophenol indicates the dissociation of its associated molecules.

The density curves (Fig. 8) are straight lines, and only the 140° isotherm is slightly convex to the compsoition axis.

The electrical conductivity curves (Fig. 9), as in the previous system, have a maximum in the region rich in urea; thus, for the 130° isotherm it is found at 80, and for the 140° isotherm at 85 mole % of urea. It might be thought that displacement of the maximum up to 85 mole % of urea occurred as the result of a lower viscosity in this region. Actually, on the electrical conductivity curves corrected for viscosity, which are shown in Fig. 10, the maximum for both the 130° and 140° isotherms is found at 80 mole % urea. In contrast to the system urea-p-nitrophenol (Fig. 5), the difference between $\eta\kappa$ maximum ($73.78 \cdot 10^4$) for 140° and $\eta\kappa$ urea ($6.86 \cdot 10^4$) is considerably greater. Partial decomposition takes place when the mixtures are heated above 150°.

System urea-2,4,6-trinitrophenol. Chemically pure picric acid was used in the study, which after recrystallization from alcohol had m.p. 121.8°.

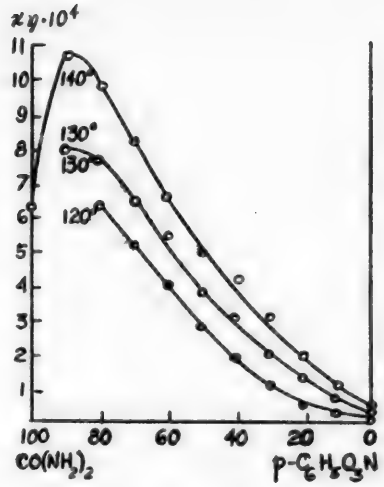

Fig. 5. Electrical conductivity curves, corrected for viscosity, of the system urea-p-nitrophenol.

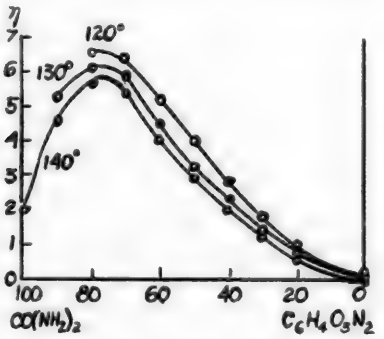

Fig. 7. Viscosity curves of the system urea-2,4-dinitrophenol.

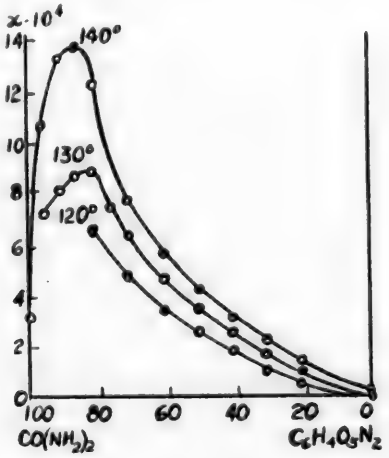

Fig. 9. Electrical conductivity curves of the system urea-2,4-dinitrophenol.

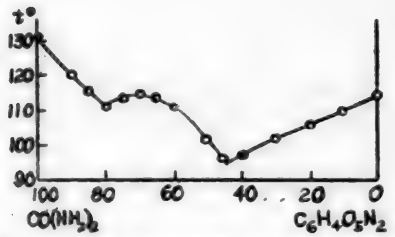

Fig. 6. Melting point curve of the system urea-2,4-dinitrophenol.

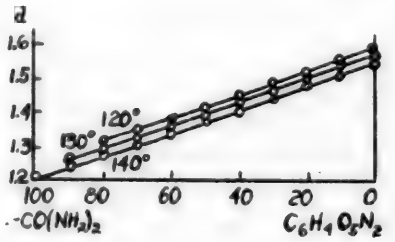

Fig. 8. Density curves of the system urea-2,4-dinitrophenol.

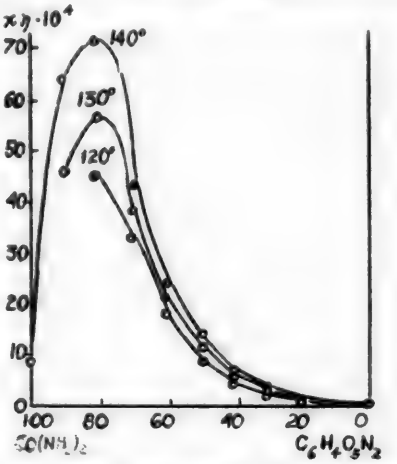

Fig. 10. Electrical conductivity curves, corrected for viscosity, of the system urea-2,4-dinitrophenol.

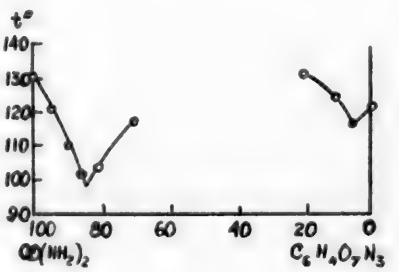

Fig. 11. Melting point curves of the system urea, 2,4,6-trinitrophenol.

We were unable to make a sufficiently full study of the melting of the system due to the fact that decomposition is encountered for the mixtures that contain from 70 to 20 mole% of urea. This situation also prevented us from studying the system in the liquid phase. Part of the melting curve is shown in Fig. 11, from which it can be seen that chemical interaction takes place in the system. The eutectics have the composition 83 and 5 mole % of urea with the corresponding melting points being 97.8 and 116.7°.

To determine the composition and melting point of the picrate we attempted to obtain the picrate by the method of mixing hot saturated water solutions of urea and picric acid. In the case where solutions containing equimolecular amounts of urea and picric acid were poured together the product obtained on cooling was picric acid; in the case where two moles (or more) of urea were taken for one mole of picric acid the precipitate obtained was a picrate with m.p. 150.6°.

0.640, 0.874 g sub.: 0.126, 0.172 g KOH [7]. Found %: $C_6H_4O_7N_3$ 80.9, 80.8. $CO(NH_2)_2 \cdot C_6H_4O_7N_3$. Calculated %: $C_6H_4O_7N_3$ 79.3.

The picrate [6] with composition 1:1, described in the literature, has m.p. 142°.

DISCUSSION OF RESULTS

A study of the systems formed by the reaction of urea with nitrobenzene, p-nitrotoluene, and o-nitrotoluene reveals that the presence of a nitro group in the aromatic nucleus leads to stratification. The tendency for mutual solubility is not increased by the introduction of a second nitro group [8].

It is known that the introduction of a nitro group into phenol results in considerably increased mobility of the hydroxyl hydrogen. A study of the system urea-p-nitrophenol revealed that chemical interaction takes place between the components with the formation of the compound $CO(NH_2)_2 \cdot C_6H_5O_3N$, finding reflection on the melting curves. This compound, judging from the viscosity curves, having a maximum in the region of 50 mole %, is also retained in the liquid phase.

The electrical conductivity curves in this system have a maximum in the region of 90 mole % urea. It should be mentioned that such a jump in electrical conductance on adding 5-15 mole % of the second component, usually with a lower electrical conductance, is also observed for those systems in which chemical interaction is not revealed by other physico-chemical analysis methods [9].

Usanovich [10] believes that such electrical conductivity curves indicate acid-base interaction. It seems to us that such a jump in electrical conductivity is not always produced by interaction in the system, but can arise as the result of increased ionic mobility produced by a certain degree of second component dilution.

If the introduction of the nitro group in the para position not only led to complete miscibility but also increased the degree of chemical interaction with urea, then the introduction of the nitro group in the ortho position (system urea-o-nitrophenol) failed to eliminate stratification in the system. That the behavior of o-nitrophenol in the system with urea is analogous to that shown by nitrobenzene is probably associated with the fact that the hydroxyl group, the presence of which should facilitate not only mutual solubility but also chemical interaction, is already bound in the nucleus due to internal hydrogen bonding.

In connection with this a study of the system urea-2,4-dinitrophenol offered much interest, inasmuch as in this case one of the nitro groups is in the ortho position and the second is in the para position to the hydroxyl group. A study of the melting point curve revealed that chemical interaction takes place in the system urea-2,4-dinitrophenol with the formation of the compound $2CO(NH_2)_2 \cdot C_6H_4O_6N_2$. The maximum on the viscosity isotherm, occurring in the region of 75 mole % urea, and on the electrical conductivity isotherm, occurring at 80 mole % of urea, confirmed the presence of this compound in the liquid phase also. It is interesting to mention that the introduction of a second nitro group in the ortho position to the hydroxyl (into p-nitrophenol) changed the composition of the obtained compound. In the system urea-2,4-dinitrophenol the prolonged heating above 150° of mixtures analyzing close to 50 mole % results in gas evolution and the formation of a high melting product that is difficultly soluble in water. An increase in the number of nitro groups to three, as was revealed in the study of the system urea-picric acid, lowers the decomposition temperature of the mixtures; thus, in the 50 mole % region it drops to 110-120°. However, the strength of the chemical union with urea is increased, inasmuch as it is possible to obtain the fairly stable picrate $CO(NH_2)_2 \cdot C_6H_3O_7N_3$.

SUMMARY

1. A study was made of the viscosity, densityy, and electrical conductivity of the systems urea-p-nitrophenol and urea-2,4-dinitrophenol at 120, 130, and 140°, and also of their melting.

2. It was established that chemical interaction is also present in the liquid phase for the system urea-p-nitrophenol with the formation of the compound $CO(NH_2)_2 \cdot C_6H_5O_3N$.

3. The presence of chemical interaction was established in the system urea-2,4-dinitrophenol with the formation of the compound $2CO(NH_2)_2 \cdot C_6H_4O_5N_2$, which found reflection on the curves of all of the investigated properties.

4. The product urea picrate $CO(NH_2)_2 \cdot C_6H_3O_7N_3$ was obtained from water with m.p. 150.6°.

5. The presence of stratification was established in the systems urea-nitrobenzene, urea-o-nitrotoluene, and urea-p-nitrotoluene.

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POLAROGRAPHIC INVESTIGATION OF HYDROGENATION PROCESSES

IV. HYDROGENATION OF ALLYL ACETATE MIXTURES WITH DI- AND TRISUBSTITUTED ETHYLENE DERIVATIVES

A. L. Markman and A. S. Gorokhovskaya

Lebedev [1], in studying the catalytic hydrogenation process for binary mixtures of unsaturated compounds, established a number of rules. In particular, he established that on all of the hydrogenation curves for mixtures, in which one of the components is a monosubstituted ethylene derivative, there occur sharply defined breaks and two more or less horizontal sections; the monosubstituted ethylene derivatives always hydrogenate first. Making use of contemporary terminology, this rule should be understood to mean that the hydrogenation of such mixtures proceeds selectively with saturation of the monosubstituted ethylene in the first phase.

We chose allyl acetate as the monosubstituted ethylene derivative for our experiments. Allyl acetate fails to give a polarographic wave. Selecting as the second component of the mixture a compound capable of being polarographed, we were able from variation in the wave height of the latter to follow the distribution of hydrogen between both components in the mixture during the whole process [2].

EXPERIMENTAL

In the experiments with allyl acetate-maleic acid and allyl acetate-fumaric acid mixtures we polarographed the samples that were taken during the hydrogenation course, for which purpose we dissolved 1 ml of each sample in 50 ml of 0.1 N HCl in 50% alcohol. In our paper [3] we have already given the conditions for polarographing maleic and fumaric acids in HCl acidified alcohol solution. Striving to separate the half-wave potentials of the two geometric isomers as much as possible during their joint polarographing, we used 95-96% alcohol in the experiments described in our paper [3]. In the present experiments with binary mixtures composed of allyl acetate with each of two stereoisomeric acids we succeeded in polarographing these acids in 50% alcohol solution. In this way for maleic acid we obtained the half-wave potential $\pi_{1/2}$ −0.68 V, and for fumaric acid −0.82 V.

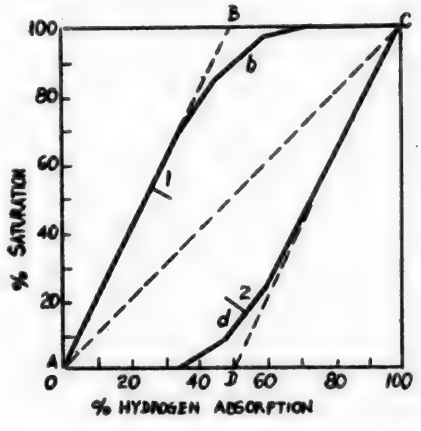

Fig. 1. Hydrogenation of allyl acetate-maleic acid mixture. Catalyst-palladium. 1) Allyl acetate, 2) Maleic acid.

In the given case, as in all of the experiments described below, the series of polarographic curves that were obtained had the same appearance as those shown in Fig. 2 of a previous paper [2]. One of these series of curves obtained by us in our experiments with allyl acetate is given below for the mixture of allyl acetate with mesityl oxide (Fig. 10).

In all of the experiments we took 50 mg of allyl acetate, 210 mg of Al, and 40 ml of alcohol for each experiment; the bath temperature was always kept at 25°.

1. Hydrogenation of allyl acetate-maleic acid mixture in the presence of palladium. The results are summarized in Table 1 and plotted in Fig. 1, where the broken diagonal AC corresponds to the completely nonselective process; the broken lines ABC and ADC correspond to the strictly selective saturation of allyl acetate in the first phase, and of maleic acid in the second phase. Actually, the saturation of allyl acetate proceeds along curve AbC, and that of maleic acid along curve AdC, i.e., with a certain deviation from strict selectivity. The index of selectivity is the ratio of the area of figure AbCdA to the area of the parallelogram ABCD. In the given case this index is S = 0.930. In a parallel experiment the value S = 0.936 was obtained.

The rate of hydrogen absorption by a mixture of allyl acetate and maleic acid is shown in Fig. 2; the arrow indicates the point at which half of the theoretical amount of hydrogen had been absorbed. As is shown by the curve, the absorption rate in the first half of the process is considerably greater than in the second half, i.e., allyl acetate is

hydrogenated much faster than maleic acid; however, contrary to the indications of Lebedev, both portions of the curve fail to be horizontal. From the character of both portions of the curve it must be assumed that the saturation of both allyl acetate nnd maleic acid is a first order reaction. The point, close to half saturation (more exactly, the point at which saturation is 46.9%), corresponds to a maleic acid concentration of $230 \cdot 10^{-5}$ mole/liter and allyl acetate concentration of $35 \cdot 10^{-5}$ mole/liter with the initial concentrations of both components being $250 \cdot 10^{-5}$ mole/liter

From this the ratio of the hydrogenation constants of the components in the mixture is equal to $K = \log \frac{C_0''}{C''} : \log \frac{C_0^*}{C^*} = 0.042$. Based on the considerations which we expressed earlier [3], for characterizing the degree of process selectivity it is more expedient to use the quantity $1-K$ as the index. In the given case this index is equal to 0.958, which is sufficiently close to the index obtained by us using the graph method; the latter should be considered as being the more accurate.

TABLE 1

Hydrogenation of Allyl Acetate-Maleic Acid Mixture in the Presence of Pd

Maleic acid 0.58 g, Pd 32 mg. Room temperature 20°. Pressure 722 mm. Theory for hydrogen absorption H_0 253 ml.

H_2 Absorption		Wave height (in mm)	Maleic Acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$ *	$\Delta C \cdot 10^{-5}$ *	Saturation (in %)	$C \cdot 10^{-5}$*	$\Delta C \cdot 10^{-5}$*	Saturation (in %)
0	0	380	250	0	0	250	0	0
27.3	10.8	380	250	0	0	196	54	21.6
56.0	22.1	380	250	0	0	139	111	44.4
86.4	34.1	380	250	0	0	79	171	68.4
118.7	46.9	350	230	20	8.0	35	215	86.0
153.3	60.6	290	191	59	23.6	0	250	100
190.3	75.2	188	124	126	50.4	0	250	100
230.1	91.0	68	45	205	82.0	0	250	100
253.0	100	0	0	250	100	0	250	100

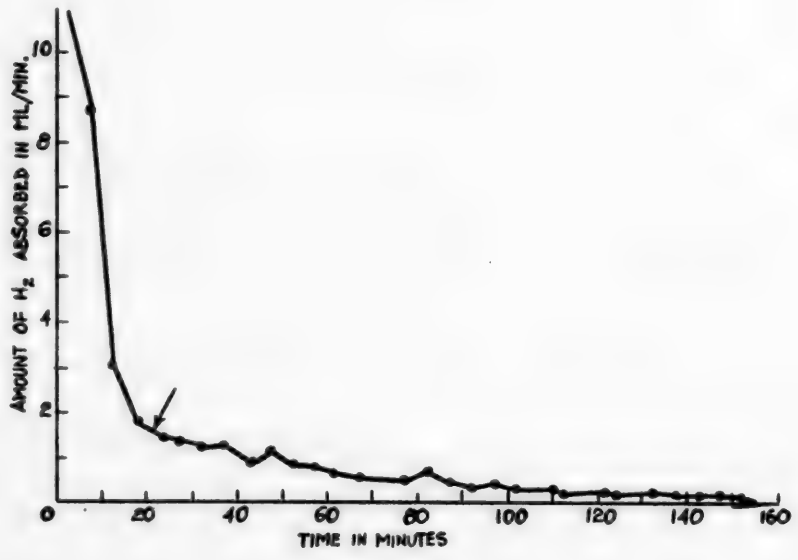

Fig. 2. Hydrogen absorption rate curve for a mixture of allyl acetate and maleic acid. Explanation in text.

* In this and in the other tables the value C designates concentration, while the value ΔC designates the drop in concentration for each of the components in the mixture. Both values are expressed in moles/liter.

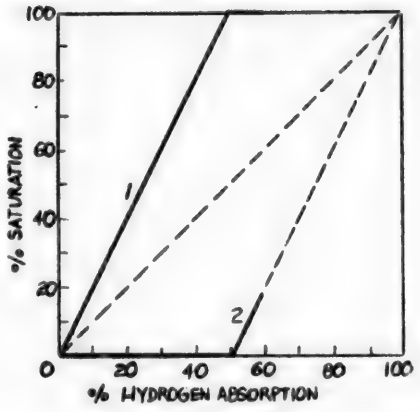

Fig. 3. Hydrogenation of allyl acetate-maleic acid mixture. Catalyst platinum.
1) Allyl acetate, 2) Maleic acid.

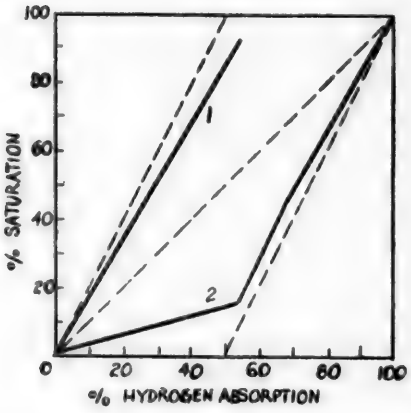

Fig. 4. Hydrogenation of allyl acetate-fumaric acid mixture. Catalyst palladium.
1) Allyl acetate, 2) Fumaric acid.

TABLE 2

Hydrogenation of Allyl Acetate-Maleic Acid Mixture in the Presence of Pt

Maleic acid 0.58 g, Pt 116 mg. Room temperature 14°. Pressure 728 mm. Theory for hydrogen absorption H_0 245.8 ml.

H_2 Absorption		Wave height	Maleic acid			Allyl acetate		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	400	250	0	0	250	0	0
21.3	8.6	400	250	0	0	207	43	17.2
43.5	17.7	400	250	0	0	162	88	35.2
67.0	27.2	400	250	0	0	114	136	54.4
92.0	37.4	400	250	0	0	63	187	74.8
118.7	48.2	400	250	0	0	9	241	96.4
145.0	59.0	330	205	45	18.0	0	250	100

2. Hydrogenation of allyl acetate-maleic acid mixture in the presence of platinum. The results are given in Table 2 and Figure 3. Without making any measurements it can be seen from the figure that the process is strictly selective: the hydrogenation of maleic acid begins after 100% saturation of allyl acetate.

3. Hydrogenation of allyl acetate-fumaric acid mixture in the presence of palladium. The results are given in Table 3 and Figure 4. From the graph we find S = 0.758. In a parallel experiment S = 0.761.

4. The hydrogenation of allyl acetate-fumaric acid mixture in the presence of platinum is shown in Table 4 and Figure 5, the character of the latter being the same as Figure 3. The degree of selectivity is S = 1.0.

5. Hydrogenation of allyl acetate-cinnamic acid mixture in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N NH_4Cl solution in 96% alcohol (Table 5 and Figure 6). For this case found S = 0.512. In a parallel experiment S = 0.528. For the sake of comparison we present the calculation of the selectivity index according to Zinovyev [4] (Table 6).

6. Hydrogenation of allyl acetate-cinnamic acid mixture in the presence of platinum. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N NH_4Cl solution in 50% ethanol (Table 7 and Figure 7). For this case found S = 0.990.

TABLE 3

Hydrogenation of Allyl Acetate-Fumaric Acid Mixture in the Presence of Pd

Fumaric acid 0.58 g, Pd 64 mg. Room temperature 19°. Pressure 726 mm. Theory for hydrogen absorption H_0 250.8 ml $\pi_{1/2}$ − 0.82 V

H_2 Absorption		Wave height (in mm)	Fumaric acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	310	250	0	0	250	0	0
21.4	9.7	300	242	8	3.2	209	41	16.4
50.0	20.0	290	234	16	6.4	167	83	33.2
77.2	30.8	280	226	24	9.6	120	130	52.0
106.0	42.3	270	218	32	12.8	71	179	71.6
136.9	54.6	260	210	40	16.0	17	233	93.2
169.9	67.7	175	141	109	43.6	12	238	95.2
205.5	82.0	104	84	166	66.4	6	244	97.6
243.3	97.0	18	15	235	94.0	0	250	100

TABLE 4

Hydrogenation of Allyl Acetate-Fumaric Acid Mixture in the Presence of Pt

Fumaric acid 0.58 g, Pt 116 mg. Room temperature 20°. Pressure 720 mm. Theory for hydrogen absorption H_0 253.8 ml.

H_2 Absorption		Wave height (in mm)	Fumaric acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	310	250	0	0	250	0	0
21.1	8.3	310	250	0	0	208	42	16.8
43.3	17.1	310	250	0	0	165	85	34.0
61.8	24.4	310	250	0	0	128	122	48.8
91.8	36.2	310	250	0	0	69	181	72.4
118.5	46.7	310	250	0	0	17	233	93.2
131.9	52.0	298	240	10	4.0	0	250	100

TABLE 5

Hydrogenation of Allyl Acetate-Cinnamic Acid Mixture in the Presence of Pd

Cinnamic acid 0.74 g, Pd 64 mg. Room temperature 20°. Pressure 731 mm. Theory for hydrogen absorption H_0 250 ml. $\pi_{1/2}$ − 1.56 V.

H_2 Absorption		Wave height (in mm)	Cinnamic acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	450	250	0	0	250	0	0
21.1	8.4	420	233	17	6.8	225	25	10.0
43.4	17.4	400	222	28	11.2	191	59	23.6
67.4	27.0	380	211	39	15.6	154	96	38.4
93.5	37.4	340	189	61	24.4	124	126	50.4
120.9	48.4	300	167	83	33.2	91	159	63.6
160.5	60.2	280	154	96	38.4	45	205	82.0
182.2	72.9	220	122	128	51.2	14	236	94.4

7. Hydrogenation of allyl acetate-itaconic acid mixture in the presence of palladium. For polarographing [5], 1 ml of each sample was dissolved in 25 ml of 0.1 N HCl in 50% ethanol (Table 8 and Figure 8). For the given case S = 0.854. In a parallel experiment obtained S = 0.845.

8. Hydrogenation of allyl acetate-itaconic acid mixture in the presence of platinum. The conditions for polarographing were the same as in the previous experiment (Table 9 and Figure 9). For the given case found S = 0.882.

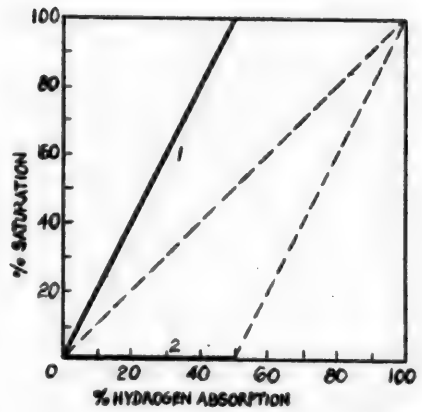

Fig. 5. Hydrogenation of allyl acetate-fumaric acid mixture. Catalyst - platinum.
1) Allyl acetate, 2) Fumaric acid.

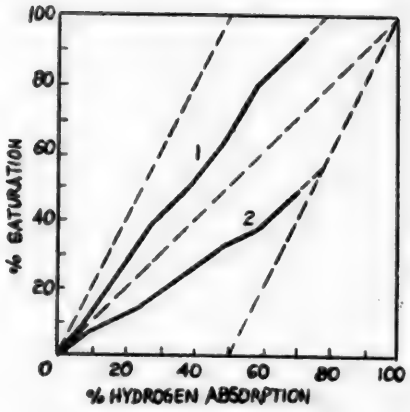

Fig. 6. Hydrogenation of allyl acetate-cinnamic acid mixture. Catalyst - palladium.
1) Allyl acetate, 2) Cinnamic acid.

TABLE 6
Calculation of the Index of Selectivity According to Zinovyev [4]

τ (min.)	Cinnamic acid, C_0 = 250			Allyl acetate, C_0 = 250			K
	C	$\frac{C_0}{C}$	$\log \frac{C_0}{C}$	C	$\frac{C_0}{C}$	$\log \frac{C_0}{C}$	
2	233	1.073	0.03060	225	1.111	0.04571	0.670
4	222	1.126	0.05154	191	1.309	0.11694	0.441
6.5	211	1.185	0.07372	154	1.623	0.21032	0.351
9	189	1.323	0.12156	124	2.016	0.30449	0.408
13.25	167	1.497	0.17522	91	2.747	0.43886	0.399
27.25	156	1.603	0.20493	45	5.556	0.74476	0.276
112.25	122	2.049	0.31154	14	17.86	1.25188	0.257
				Average		0.400	

Index of selectivity 1−K = 0.600

Next we hydrogenated a mixture of allyl acetate with the trisubstituted ethylene derivative – mesityl oxide. As regards the polarographic behavior of mesityl oxide we found only one reference in the literature: according to Adkins and Cox [6], mesityl oxide gives a wave with a half-wave potential of −1.61V, in aqueous NH_4Cl solution and −1.64 V in $N(CH_3)_4OH$.

The polarographing of mesityl oxide was made in 0.1 N NH_4Cl in 50% ethanol. Under these conditions mesityl oxide gives a well defined polarographic wave with a half-wave potential of −1.40 V. The relationship between the wave height and concentration is shown in Table 10.

The values given in Table 10 indicate that a direct relationship exists between the diffusion current and the concentration of the solution.

If should be mentioned that in contrast to cinnamic acid, mesityl oxide fails to give a polarographic wave in a pure alcohol solution of ammonium chloride.

9. Hydrogenation of allyl acetate-mesityl oxide mixture in the presence of palladium. 1 ml of each sample was

dissolved in 50 ml of 0.1 N NH_4Cl in 50% ethanol. The obtained polarograms are shown in Fig. 10, while the results are given in Table 11 and Figure 11. As can be seen from the graph, the index of selectivity is S = 1.0.

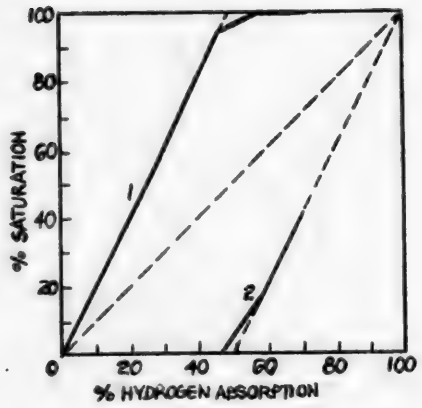

Fig. 7. Hydrogenation of allyl acetate-cinnamic acid mixture. Catalyst platinum.
1) Allyl acetate, 2) Cinnamic acid.

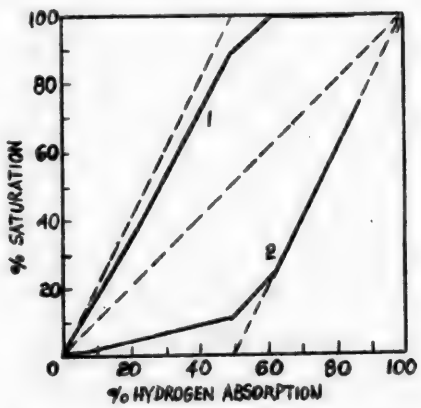

Fig. 8. Hydrogenation of allyl acetate-itaconic acid mixture. Catalyst palladium.
1) Allyl acetate, 2) Itaconic acid.

TABLE 7

Hydrogenation of Allyl Acetate-Cinnamic Acid Mixture in the Presence of Pt
Cinnamic acid 0.74 g, Pt 116 mg. Room temperature 19°. Pressure 725 mm. Theory for hydrogen absorption H_0 251.4 ml. $\pi_{1/2}$ −1.51 V.

H_2 Absorption		Wave height (in mm)	Cinnamic acid			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	300	250	0	0	250	0	0
21.1	8.4	300	250	0	0	208	42	16.8
43.3	17.2	300	250	0	0	164	86	34.4
66.8	26.6	300	250	0	0	117	133	53.2
91.8	36.5	300	250	0	0	67	183	73.2
118.5	47.1	300	250	0	0	13	237	94.8
147.1	58.5	250	208	42	16.8	0	250	100
177.9	70.8	175	146	104	41.6	0	250	100

10. Hydrogenation of allyl acetate-mesityl oxide mixture in the presence of platinum. The conditions for polarographing were the same as in the previous experiment (Table 12 and Figure 12). For this case S = 0.933.

From an examination of the above experiments it is seen that, in accord with the Lebedev rule, allyl acetate in all cases suffers preferential hydrogenation over di- and trisubstituted ethylene derivatives. However, this preference does not always grow into absolute selectivity.

In mixtures with maleic, fumaric and cinnamic acids the hydrogenation of allyl acetate is absolutely selective in the presence of platinum; in the presence of palladium both components of the mixture suffer simultaneous hydrogenation; however, the hydrogenation rate for allyl acetate is much faster than it is for the disubstituted ethylenic acids. The hydrogenation of allyl acetate-itaconic acid mixtures in the presence of either palladium or platinum bears a similar strictly selective character. In mixtures with the trisubstituted ethylene derivative, mesityl oxide, the hydrogenation of allyl acetate is strictly selective in the presence of palladium and shows a slight deviation from absolute selectivity in the presence of platinum.

TABLE 8

Hydrogenation of Allyl Acetate-Itaconic Acid Mixture in the Presence of Pd

Itaconic acid 0.65 g, Pd 64 mg. Room temperature 12°. Pressure 729.0 mm. Theory for hydrogen absorption H_0 243.8 ml. $\pi_{1/2}$ −0.79 V

H_2 Absorption		Wave height	Itaconic acid			Allyl acetate		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	220	500	0	0	500	0	0
21.9	9.0	215	489	11	2.2	421	79	15.8
46.1	18.9	210	477	23	4.6	334	166	33.2
70.8	29.0	205	466	34	6.8	244	256	51.2
95.8	39.2	200	455	45	9.0	152	348	69.6
122.5	50.2	195	443	57	11.4	55	445	89.0
155.1	61.9	167	380	120	24.0	0	500	100
181.9	74.5	112	254	246	49.2	0	500	100
214.2	87.8	54	122	378	75.6	0	500	100

TABLE 9

Hydrogenation of Allyl Acetate-Itaconic Acid Mixture in the Presence of Pt

Itaconic acid 0.65 g, Pt 140 mg. Room temperature 14°. Pressure 723.5 mm. Theory for hydrogen absorption H_0 247.4 ml.

H_2 Absorption		Wave height	Itaconic acid			Allyl acetate		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	220	500	0	0	500	0	0
27.9	11.3	220	500	0	0	387	113	22.6
56.0	22.7	210	477	23	4.6	297	203	40.6
85.8	34.7	205	466	34	6.8	179	321	64.2
117.8	47.6	200	455	45	9.0	69	431	86.2
150.9	61.0	172	390	110	22.0	0	500	100
186.4	75.4	108	247	253	50.6	0	500	100
224.4	90.8	41	93	407	81.4	0	500	100
231.6	93.6	28	64	436	87.2	0	500	100

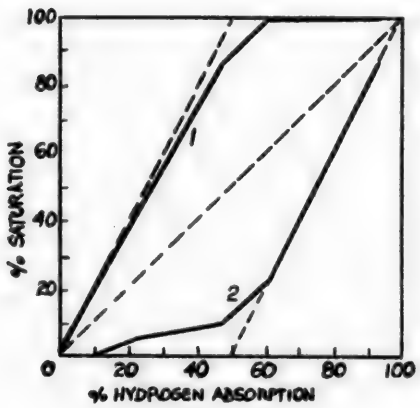

Fig. 9. Hydrogenation of allyl acetate-itaconic acid mixture. Catalyst - platinum
1) Allyl acetate, 2) Itaconic acid.

TABLE 10

Polarographic Indices of Mesityl Oxide

$C \cdot 10^{-3}$ (mole/liter)	h (in mm)	$\frac{h}{C} \cdot 10^4$
5	180	2.6
1	28	2.8
0.5	14	2.8
	Average	2.73

TABLE 11

Hydrogenation of Allyl Acetate-Mesityl Oxide Mixture in the Presence of Pd

Mesityl oxide 0.49 g, Pd 64 mg. Room temperature 12°. Pressure 723 mm. Theory for hydrogen absorption H_0 246 ml. $\pi_{1/2}$ −1.37 V.

H_2 Absorption		Wave height (in mm)	Mesityl oxide			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	95	250	0	0	250	0	0
27.3	11.1	95	250	0	0	195	55	22.0
57.1	23.2	95	250	0	0	134	116	46.4
89.1	36.2	95	250	0	0	69	181	72.4
122.4	49.8	95	250	0	0	1	249	99.6
159.3	64.8	67	177	73	29.2	0	250	100
197.5	89.2	38	99	151	60.4	0	250	100
238.3	96.9	6	16	234	93.6	0	250	100
246.3	100	0	0	250	100	0	250	100

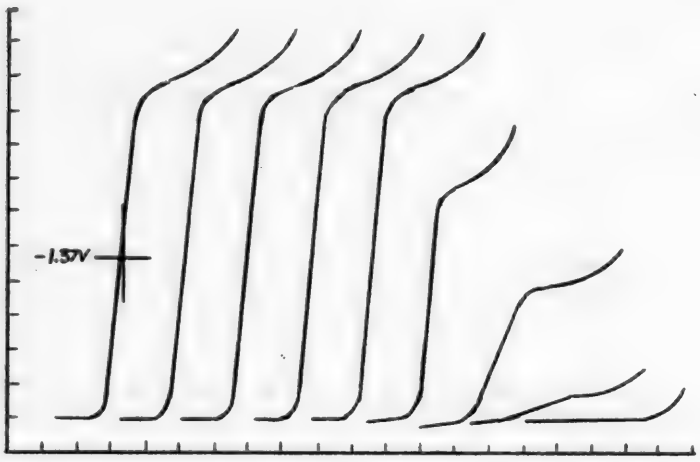

Fig. 10. Hydrogenation polarograms of allyl acetate-mesityl oxide mixture. Catalyst palladium.

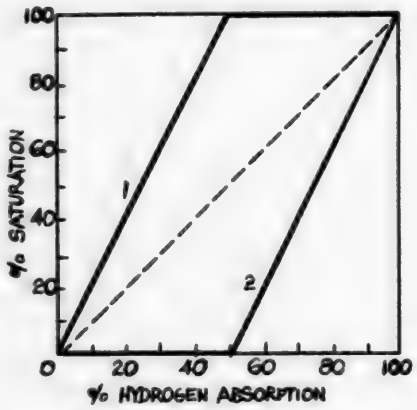

Fig. 11. Hydrogenation of allyl acetate-mesityl oxide mixture. Catalyst palladium.
1) Allyl acetate, 2) Mesityl oxide.

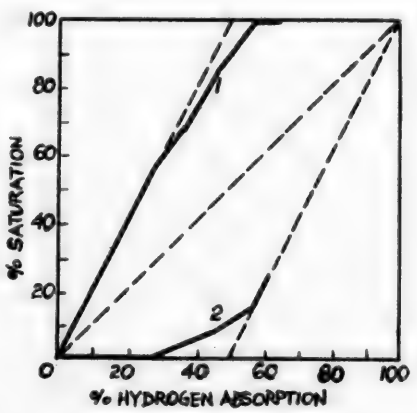

Fig. 12. Hydrogenation of allyl acetate-mesityl oxide mixture. Catalyst platinum.
1) Allyl acetate, 2) Mesityl oxide.

TABLE 12

Hydrogenation of Allyl Acetate-Mesityl Oxide Mixture in the Presence of Pt

Mesityl oxide 0.49 g, Pt 116 mg. Room temperature 25°. Pressure 720 mm. Theory for hydrogen absorption H_0 252.9 ml

H_2 Absorption		Wave height (in mm)	Mesityl oxide			Allyl acetate		
ml	%		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (in %)
0	0	120	250	0	0	250	0	0
21.1	8.3	120	250	0	0	209	41	16.4
43.3	17.1	120	250	0	0	164	86	34.4
66.8	26.4	120	250	0	0	118	132	52.8
91.8	36.3	115	239	11	4.4	80	170	68.0
118.5	46.8	110	229	21	8.4	37	213	85.2
147.1	58.2	101	210	40	16.0	0	250	100
157.3	62.2	91	189	61	24.4	0	250	100

SUMMARY

1. With the aid of the polarographic method the hydrogenation processes for binary mixtures of allyl acetate with certain di- and trisubstituted ethylene derivatives were studied. It was established that the Lebedev rule relative to the preferential saturation of the monosubstituted ethylene derivative in the first phase is a first approximation generalization. Depending on the nature of the second component in the mixture and on the catalyst, the degree of selective saturation of the monosubstituted ethylene derivative fluctuates within fairly wide limits (in our experiments from 0.512 to 1.00).

2. The conditions for polarographing mesityl oxide were established, making possible its quantitative determination in solutions.

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Central Asian Polytechnical Institute

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POLAROGRAPHIC INVESTIGATION OF THE HYDROGENATION PROCESS

V. HYDROGENATION OF MIXTURES OF DISUBSTITUTED ETHYLENE DERIVATIVES

A. L. Markman

According to Lebedev's observations [1], the symmetrical disubstituted ethylene derivatives are divided into two groups according to their behavior during catalytic hydrogenation: those compounds which, under the conditions of the experiment, are saturated at relatively high rates (11-20 ml of H_2 per minute), and those for which the rate of saturation is considerably less (2-4 ml per minute). To this last category belong compounds in which the double bond is in bilateral conjugation to the benzene ring or to carboxyl. Similar observations were made by Adams [2], Adkins [3] and Kazansky [4].

Of the number of symmetrical disubstituted ethylene derivatives, we studied maleic, fumaric, cinnamic and oleic acids. Hydrogenation experiments of all these acids were carried out under the same conditions: catalyst in the quantity of 32 mg of Pd or 58 mg of Pt per 0.005 mole of acid was introduced; the bath temperature was 25°. We described the technique of hydrogenation, the selection of sample and the polarographic control of the course of saturation earlier [5]. Rate of saturation constants were calculated for each object of investigation from the equation of a first order reaction (Table 1).

Thus, the figures of Table 1 bear out the observations of other authors concerning the fact that oleic acid differs from the other three acids by its considerably higher rate of saturation.

TABLE 1

Reaction Rate Constants of the Catalytic Hydrogenation of Acids

Acids	Catalyst	
	Pd	Pt
Maleic	0.0468	0.0190
Fumaric	0.0067	0.0095
Cinnamic	0.0435	0.0123
Oleic	0.2136	0.0737

Turning to the problem of the hydrogenation of binary mixtures of disubstituted ethylenes, we note the work of Lebedev [1], Yurashevsky [6], Ipatyev [7], Bogdanov and Bashkirova [8], carried out in this direction.

Because of the essential difference of oleic acid from the other three above-named acids, with respect to the nature of substituents, we studied the behavior of binary mixtures, one of the components of which was oleic acid.

If we measure the activity of the double bond by the rate of its saturation, then it can be expected that in mixtures of oleic and maleic acids the oleic will be selectively saturated first. If we assume that both acids are saturated simultaneously, each at its inherent rate, then in this case also the oleic acid should be saturated more rapidly than the maleic. However, the experiment gave no such results.

EXPERIMENTAL

In all the experiments described below we used 210 mg of Al as the carrier, and 40 ml of alcohol as the solvent (with the exception of two experiments); the bath temperature, with the exception of certain indicated cases, was 40°.

1. Hydrogenation of a mixture of oleic and maleic acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 96% ethanol [9] (Table 2, Fig. 1). For this experiment an index of selectivity of S = 0.969 was found.

2. Hydrogenation of a mixture of oleic and maleic acids in the presence of platinum. The conditions of polarographing were the same as in the preceding experiment (Table 3, Fig. 2). The index of selectivity was S = 0.609.

Thus, we see that the palladium catalyst specifies strict selectivity of the process of hydrogenation of mixtures of maleic and oleic acids, with saturation of the maleic acid first, and this occurs in spite of the fact that during a separate hydrogenation oleic acid is saturated incomparably more rapidly than is maleic. In the presence of a

TABLE 2

Hydrogenation of a Mixture of Oleic and Maleic Acids in the Presence of Pd
Oleic acid 1.41 g, maleic acid 0.58 g; Pd 64 mg. Temperature of the air 18°. Pressure 721.5 mm. Theoretical absorption of hydrogen H_0 251.5 ml. $\pi_{1/2}$ −0.76 v

Absorption of H_2		Wave height	Maleic acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	575	250	0	0	250	0	0
26.9	10.7	453	197	53	21.2	250	0	0
56.0	22.2	320	139	111	44.4	250	0	0
85.9	34.1	182	79	171	68.4	250	0	0
117.2	46.6	60	26	224	89.6	241	9	3.6
151.3	60.1	0	0	250	100	199	51	20.4
187.0	74.3	0	0	250	100	128	122	48.8
218.7	86.9	0	0	250	100	65	185	74.0

TABLE 3

Hydrogenation of a Mixture of Oleic and Maleic Acids in the Presence of Pt
Oleic acid 1.41 g, maleic acid 0.58 g, Pt 116 mg. Temperature of the air 16°. Pressure 716.5 mm. Theoretical absorption of hydrogen H_0 251.5 ml.

Absorption of H_2		Wave height	Maleic acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	600	250	0	0	250	0	0
21.5	8.5	514	214	36	14.4	243	7	2.8
43.0	17.4	420	175	75	30.0	238	12	4.8
67.7	26.9	317	132	118	47.2	234	16	6.4
93.0	37.0	250	104	146	58.4	211	39	15.6
119.7	47.6	197	82	168	67.2	180	70	28.0
148.3	58.9	132	55	195	78.0	150	100	40.0
179.7	71.4	46	19	231	92.4	124	126	50.4
215.0	85.5	0	0	250	100	73	177	70.8
230.6	91.6	0	0	250	100	41	209	83.6

platinum catalyst both components of the mixture are saturated during the first minutes of the process; however, maleic acid is saturated at a greater rate than is oleic; therefore, the saturation of maleic acid is completed earlier than that of oleic. Thus, although not strictly maintained, in this case the process has a selective character.

3. Hydrogenation of a mixture of oleic and fumaric acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 50% ethanol [10] (Table 4, Fig. 3).

It is evident from Fig. 3 that the points characterizing the degree of saturation of fumaric and oleic acids, are located along the diagonal and along both its sides. Thus, it can be assumed that both acids are hydrogenated simultaneously and at the same rates, i.e., that essentially the process proceeds non-selectively.

Beginning the experiment with cinnamic acid, we should establish its polarographic behavior. Kolthoff and Lingane [11] cited the following data on this point: the reduction potential E in 1 N HCl in an aqueous medium (according to Shvaer) was −0.96 v; in 0.1 N NH_4Cl in 50% ethanol (according to Semerano and Chizini) it was −1.46 v. Heyrovsky [12] gave the reduction potential of cinnamic acid in an acid medium (pH 1.5) as −1.10, and in a neutral medium as −1.80 v. In later work [13] the same author cited the reduction potential of cinnamic acid in 0.1 N NH_4Cl in 50% ethanol as −0.78 v (with respect to the normal calomel electrode).

• In this and in the other tables the symbol C designates concentration, and the symbol ΔC designates the decrease of concentration of each of the components of the mixture. Both values are expressed in moles/liter.

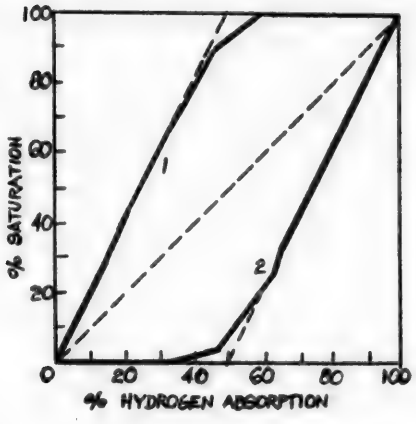


Fig. 1. Hydrogenation of a mixture of maleic and oleic acids. Catalyst palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) oleic.

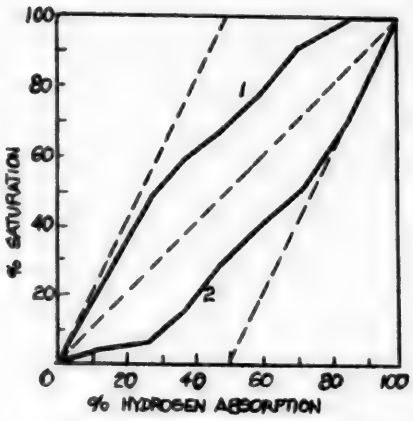


Fig. 2. Hydrogenation of a mixture of maleic and oleic acids. Catalyst-platinum.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) oleic.

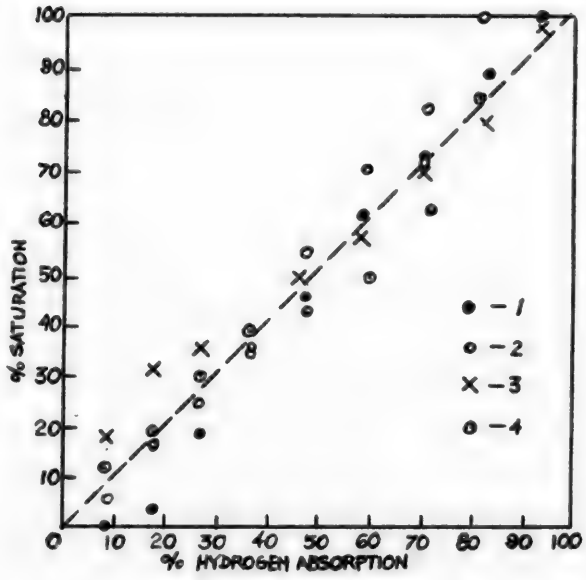


Fig. 3. Hydrogenation of a mixture of fumaric and oleic acids. Catalyst palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
1) and 2) Fumaric acid; 3) and 4) oleic acid.

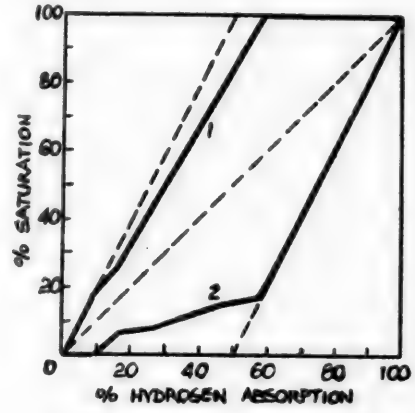


Fig. 4. Hydrogenation of a mixture of cinnamic and oleic acids. Catalyst palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) cinnamic; 2) oleic.

We carried out experiments on the polarographing of cinnamic acid in alcoholic (96%) and in alcohol-water (50%) solutions, using 0.1 N HCl or 0.1 N NH_4Cl as the inert electrolyte. In this way it was found:

1) cinnamic acid gave no polarographic waves in acidic alcoholic and in alcohol-water media;

2) a wave with a half-wave potential of −1.60 v was obtained in 0.1 N alcoholic solutions of NH_4Cl, and in alcohol-water solutions it was −1.71 v (with respect to the saturated calomel electrode);

3) there exists a strict proportionality between the diffusion current and the concentration of cinnamic acid in solution within the concentration range of $1 \cdot 10^{-5}$–$1 \cdot 10^{-3}$ mole/liter.

TABLE 4

Hydrogenation of a Mixture of Fumaric and Oleic Acids in the Presence of Pd
Oleic acid 1.41 g, fumaric acid 0.58 g, Pd 64 mg. Temperature of the air 18°. Pressure 724 mm. Theoretical absorption of hydrogen H_0 250.6 ml. $\pi_{1/2}$ −0.94 v

Absorption of H_2		Wave height	Fumaric acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	280	250	0	0	250	0	0
21.1	8.4	280	250	0	0	208	42	16.8
43.3	17.4	270	241	9	3.6	173	77	30.8
66.8	26.7	230	205	45	18.0	162	88	35.2
91.8	36.6	185	165	85	34.0	152	98	39.2
118.5	47.3	155	138	112	44.8	126	124	49.6
147.1	58.7	110	98	152	60.8	109	141	56.4
177.9	71.0	78	70	180	72.0	75	175	70.0
210.6	84.1	32	29	221	88.4	51	199	79.6
237.0	94.6	0	0	250	100	27	223	89.2
250.6	100	0	0	250	100	0	250	100

TABLE 5

Hydrogenation of a Mixture of Oleic and Cinnamic Acids in the Presence of Pd
Oleic acid 1.41 g, cinnamic acid 0.74 g, Pd 64 mg. Temperature of air 16°. Pressure 720 mm. Theoretical absorption of hydrogen H_0 250.3 ml. $\pi_{1/2}$ −1.60 v

Absorption of H_2		Wave height	Cinnamic acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	400	250	0	0	250	0	0
21.1	8.4	333	208	42	16.8	250	0	0
43.3	17.3	290	181	69	27.6	233	17	6.8
66.8	26.7	220	137	113	45.2	229	21	8.4
91.8	36.7	155	97	153	61.2	221	29	11.6
118.5	47.4	80	50	200	80.0	213	37	14.8
147.1	58.8	0	0	250	100	206	44	17.6
177.9	71.1	0	0	250	100	144	106	42.4
209.6	83.8	0	0	250	100	81	169	67.6

Employing this condition, we carried out the following experiments.

4. Hydrogenation of a mixture of oleic and cinnamic acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N NH_4Cl in 96% ethanol and the stearic acid which precipitated was filtered off (Table 5, and Fig. 4). For the present case S = 0.810 was found.

5. Hydrogenation of a mixture of oleic and cinnamic acids in the presence of platinum. The conditions of polarographing were the same as in the preceding experiment (Table 6, and Fig. 5). S = 0.829 was found.

As is evident from these experiments, the saturation of cinnamic acid proceeds preferably, although not strictly selectively, in the presence of palladium; in the presence of platinum, saturation of oleic acid is preferable.

Further, we carried out a series of hydrogenation experiments of binary mixtures of maleic and cinnamic acids. The polarographic analysis of these mixtures was based on the fact that, in acidic alcoholic and alcohol-water solutions of cinnamic acid, as noted above, no waves are produced; under these conditions maleic acid does give a clearly expressed wave.

6. Hydrogenation of a mixture of maleic and cinnamic acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 50% ethanol (Table 7, Fig. 6); the results of two experiments are reproduced in the figure). Here it is possible to assume that S = 0.

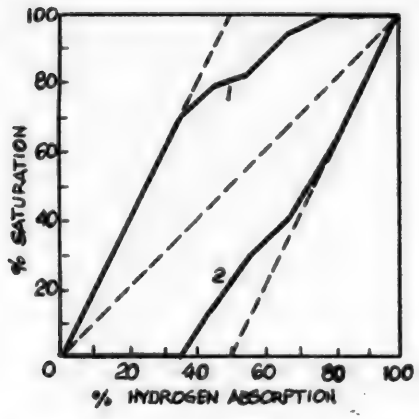


Fig. 5. Hydrogenation of a mixture of cinnamic and oleic acids. Catalyst – platinum.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) oleic; 2) cinnamic.

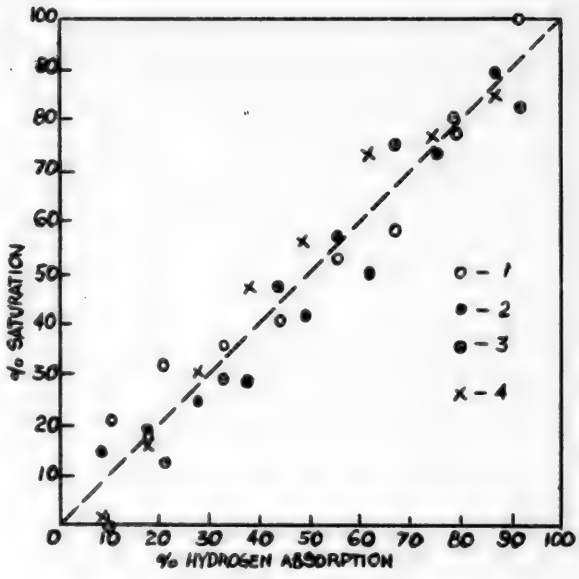


Fig. 6. Hydrogenation of a mixture of maleic and cinnamic acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
1) and 2) Maleic acid; 3 and 4) cinnamic acid.

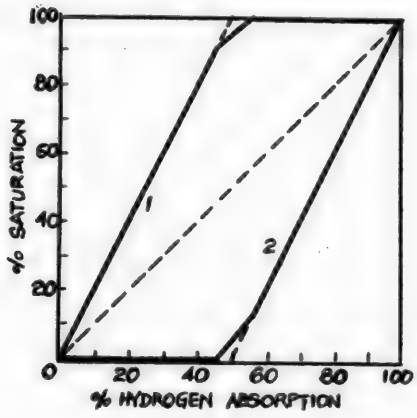


Fig. 7. Hydrogenation of a mixture of maleic and cinnamic acids. Catalyst – platinum.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) cinnamic.

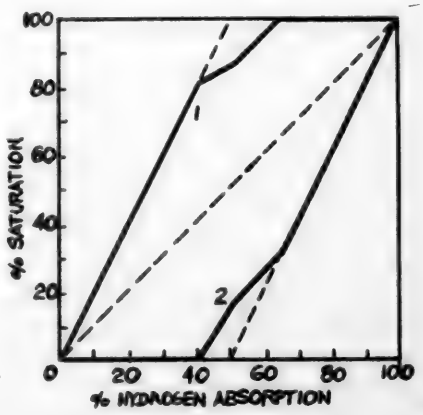


Fig. 8. Hydrogenation of a mixture of cinnamic and fumaric acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) cinnamic; 2) fumaric.

7. Hydrogenation of a mixture of maleic and cinnamic acids, in the presence of platinum. The conditions of polarographing were the same as in the preceding experiment (Table 8, Fig. 7). S = 0.988. Similar results were obtained in a different experiment carried out at a bath temperature of 25°.

Thus, the hydrogenation of mixtures of maleic and cinnamic acids in the presence of palladium proceeds entirely non-selectively; in the presence of platinum it proceeds strictly selectively, with the saturation of maleic acid first.

TABLE 6

Hydrogenation of a Mixture of Oleic and Cinnamic Acids in the Presence of Pt

Oleic acid 1.41 g, cinnamic acid 0.74 g; Pt 116 mg. Temperature of air 28°. Pressure 716.5 mm. Theoretical absorption of hydrogen H_0 262 ml.

Absorption of H_2		Wave height	Cinnamic acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	625	250	0	0	250	0	0
21.1	8.0	625	250	0	0	210	40	16.0
43.3	16.5	625	250	0	0	167	83	33.2
66.8	25.5	625	250	0	0	122	128	51.2
91.8	35.0	625	250	0	0	75	175	70.0
118.5	45.2	555	222	28	11.2	52	198	79.2
147.5	56.1	440	176	74	29.6	43	207	82.8
177.9	67.9	370	148	102	40.8	12	238	95.2
210.6	80.4	245	98	152	60.8	0	250	100
243.7	93.0	88	35	215	86.0	0	250	100

TABLE 7

Hydrogenation of a Mixture of Maleic and Cinnamic Acids in the Presence of Pd

Maleic acid 0.58 g, cinnamic acid 0.74 g, Pd 64 mg. 30 ml of alcohol and 10 ml of water. Bath temperature 25°, air 20°. Pressure 725 mm. Theoretical absorption of hydrogen H_0 252 ml. $\pi_{1/2}$ −0.73 v

Absorption of H_2		Wave height	Maleic acid			Cinnamic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	470	250	0	0	250	0	0
26.3	10.4	372	198	52	20.8	250	0	0
52.6	20.9	320	170	80	32.0	218	32	12.8
82.9	32.9	300	160	90	36.0	176	74	29.6
110.9	44.0	280	149	101	40.4	131	119	47.6
139.5	55.4	220	117	133	53.2	106	144	57.6
168.9	67.0	195	104	146	58.4	61	189	75.6
199.2	79.0	105	56	194	77.6	49	201	80.4
230.4	91.4	0	0	250	100	43	207	82.8

TABLE 8

Hydrogenation of a Mixture of Maleic and Cinnamic Acids in the Presence of Pt

Maleic acid 0.58 g, cinnamic acid 0.74 g, Pt 116 mg; temperature of air 27°. Pressure 714.5 mm. Theoretical absorption of hydrogen H_0 261.8 ml.

Absorption of H_2		Wave height	Maleic acid			Cinnamic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	1012	250	0	0	250	0	0
21.4	8.2	845	209	41	16.4	250	0	0
43.3	16.5	675	167	83	33.2	250	0	0
66.8	25.5	495	122	128	51.2	250	0	0
93.0	35.5	290	72	178	79.2	250	0	0
119.7	45.7	85	21	229	91.6	250	0	0
148.3	56.6	0	0	250	100	217	33	13.2
179.1	68.4	0	0	250	100	158	92	36.8
212.4	81.1	0	0	250	100	94	156	62.4
230.6	88.1	0	0	250	100	60	190	76.0

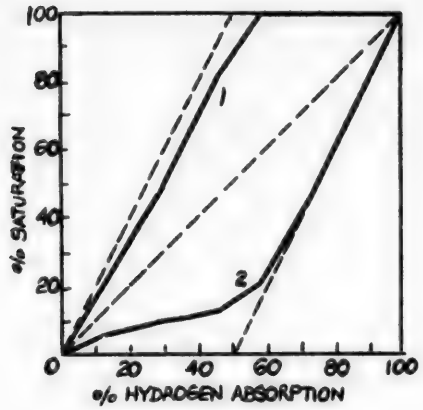


Fig. 9. Hydrogenation of a mixture of oleic and itaconic acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) oleic; 2) itaconic.

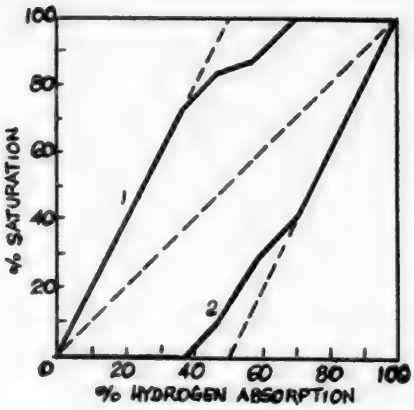


Fig. 10. Hydrogenation of a mixture of maleic and itaconic acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) itaconic.

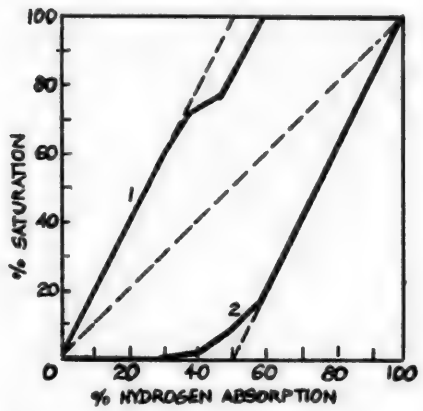


Fig. 11. Hydrogenation of a mixture of maleic and itaconic acids. Catalyst – platinum.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) maleic; 2) itaconic.

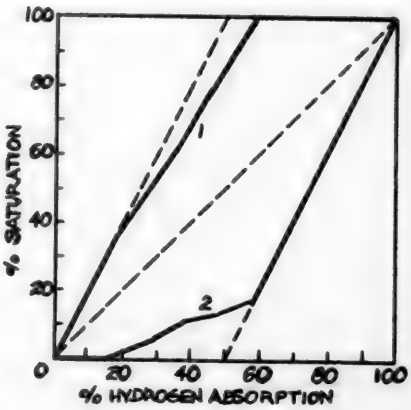


Fig. 12. Hydrogenation of a mixture of cinnamic and itaconic acids. Catalyst – palladium.
A) Per cent of saturation; B) per cent absorption of hydrogen.
Acids: 1) cinnamic; 2) itaconic.

8. Hydrogenation of a mixture of fumaric and cinnamic acids in the presence of palladium. For analysis, 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 50% ethanol; under these conditions fumaric acid polarographed, but cinnamic acid did not polarograph. (Table 9, Fig. 8). For the present case S = 0.923 was found.

All the hydrogenation experiments of mixtures of fumaric and cinnamic acids in the presence of a platinum catalyst were found to be unsuccessful, in the sense that the process stopped spontaneously long before its completion. We cite the characteristics pertaining to one such experiment.

9. Hydrogenation of a mixture of fumaric and cinnamic acids in the presence of platinum. The conditions of polarographing were the same as in the preceding experiment (Table 10).

Thus, in the presence of palladium cinnamic acid was first and almost strictly selectively hydrogenated; in the presence of platinum, as can be seen even from the uncompleted experiments, fumaric acid was saturated first.

TABLE 9

Hydrogenation of a Mixture of Fumaric and Cinnamic Acids in the Presence of Pd

Fumaric acid 0.58 g, cinnamic acid 0.74 g, Pd 64 mg, 30 ml of alcohol and 10 ml of water. Temperature of air 16°. Pressure 723 mm. Theoretical absorption of hydrogen H_0 249.2 ml. $\pi_{1/2}$ −0.90 v

Absorption of H_2		Wave height	Fumaric acid			Cinnamic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	350	250	0	0	250	0	0
23.0	9.2	350	250	0	0	204	46	18.4
48.0	19.3	350	250	0	0	154	96	38.4
73.6	29.5	350	250	0	0	102	148	59.2
100.9	40.5	350	250	0	0	48	202	80.8
130.5	52.4	288	205	45	18.0	33	217	86.8
162.6	65.3	244	174	76	30.4	0	250	100
197.8	79.4	147	105	145	58.0	0	250	100
234.9	94.3	41	29	221	88.4	0	250	100
249.4	100	0	0	250	100	0	250	100

TABLE 10

Hydrogenation of a Mixture of Fumaric and Cinnamic Acids in the Presence of Pt

Fumaric acid 0.58 g, cinnamic acid 0.74 g, Pt 116 mg. Temperature of air 27°. Pressure 713.5 mm. Theoretical absorption of hydrogen H_0 262.5 ml.

Absorption of H_2		Wave height	Fumaric acid			Cinnamic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	875	250	0	0	250	0	0
29.1	11.1	680	195	55	22.0	250	0	0
46.4	17.7	565	162	88	35.2	250	0	0
72.5	27.7	390	112	138	55.2	250	0	0
97.5	37.2	225	64	186	74.4	250	0	0
105.8	40.4	170	48	202	80.8	250	0	0

TABLE 11

Hydrogenation of a Mixture of Itaconic and Oleic Acids in the Presence of Pd

Itaconic acid 0.65 g, oleic acid 1.41 g, Pd 64 mg. Temperature of air 16°. Pressure 722 mm. Theoretical absorption of hydrogen H_0 249.6 ml. $\pi_{1/2}$ −0.85 v

Absorption of H_2		Wave height	Itaconic acid			Oleic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	470	500	0	0	500	0	0
21.1	8.4	450	479	21	4.2	436	64	12.8
43.3	17.3	440	468	32	6.4	359	141	28.2
66.8	26.7	430	457	43	8.6	276	224	44.8
91.8	36.7	420	447	53	10.6	186	314	62.8
118.7	47.3	410	436	64	12.8	89	411	82.2
147.6	59.0	371	395	105	21.0	0	500	100
173.4	71.3	269	286	214	42.8	0	500	100
211.7	84.7	144	153	347	69.4	0	500	100
224.5	89.8	96	102	398	79.6	0	500	100

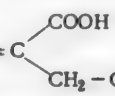
We used itaconic acid  as a representative of the group of asymmetrical disubstituted ethylene derivatives, the polarographic behavior of which we studied earlier [14].

TABLE 12

Hydrogenation of a Mixture of Maleic and Itaconic Acids in the Presence of Pd

Maleic acid 0.58 g, itaconic acid 0.65 g, Pd 64 mg. Bath temperature 25°, air 17°. Pressure 720 mm. Theoretical absorption of hydrogen H_0 251.2 ml. $\pi_{1/2}$ −1.44 v

Absorption of H_2		Wave height	Maleic acid			Itaconic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	875	500	0	0	500	0	0
21.1	8.4	728	416	84	16.8	500	0	0
43.3	17.3	572	327	173	34.6	500	0	0
66.6	26.5	411	235	265	53.0	500	0	0
91.6	36.5	236	135	365	73.0	500	0	0
118.3	47.1	145	83	417	83.4	446	54	10.8
147.4	58.7	100	57	443	88.6	356	144	28.8
178.2	71.0	0	0	500	100	290	210	42.0
205.9	82.0	0	0	500	100	180	320	64.0

TABLE 13

Hydrogenation of a Mixture of Maleic and Itaconic Acids in the Presence of Pt

Maleic Acid 0.58 g, itaconic acid 0.65 g, Pt 116 mg. Bath temperature 26°, air 26°. Pressure 722 mm. Theoretical absorption of hydrogen H_0 253.7 ml

Absorption of H_2		Wave height	Maleic acid			Itaconic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	420	250	0	0	250	0	0
22.2	8.7	340	206	44	17.6	250	0	0
44.3	17.4	272	163	87	34.8	250	0	0
68.1	26.8	193	116	134	53.6	250	0	0
93.1	36.7	115	69	181	72.4	247	3	1.2
119.8	47.2	52	31	219	87.6	233	17	6.8
148.4	58.5	0	0	250	100	207	43	17.2
179.2	70.6	0	0	250	100	147	103	41.2
202.5	79.8	0	0	250	100	101	149	59.6

TABLE 14

Hydrogenation of a Mixture of Itaconic and Cinnamic Acids in the Presence of Pd

Itaconic acid 0.65 g, cinnamic acid 0.74 g; 64 mg Pd. Bath temperature 25°, air 17°. Pressure 722 mm. Theoretical absorption of hydrogen H_0 250.4 ml. $\pi_{1/2}$ −0.82 v

Absorption of H_2		Wave height	Itaconic acid			Cinnamic acid		
ml	%	(in mm)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	saturation (in %)
0	0	190	500	0	0	500	0	0
42.5	17.0	190	500	0	0	330	170	34.0
66.7	26.6	180	474	26	5.2	260	240	48.0
92.4	36.9	170	448	52	10.4	183	317	63.4
118.9	47.5	165	434	66	13.2	91	409	81.3
146.9	58.7	157	413	87	17.4	0	500	100
175.8	70.2	113	298	202	40.4	0	500	100
206.6	82.5	67	175	325	65.0	0	500	100
209.6	83.7	62	163	337	67.4	0	500	100

10. Hydrogenation of a mixture of itaconic acid and oleic acids in the presence of palladium. For polarographing, 1 ml of each sample was dissolved in 25 ml of 0.1 N HCl in 96% ethanol (Table 11, Fig. 9). The index of selectivity was S = 0.808.

11. Hydrogenation of a mixture of maleic and itaconic acids in the presence of palladium. For polarographing, a buffer of 25 ml of 0.2 M (H_3BO_3 + KCl), 10.65 ml of 0.2 N NaOH and 64.35 ml of water was prepared; its pH was 9.00. 1 ml of each sample was dissolved in 25 ml of the buffer. Itaconic acid produced no polarographic waves, but maleic acid also polarographed in an alkaline medium [15]. (Table 12, Fig. 10). S = 0.883 was found.

12. Hydrogenation of a mixture of maleic and itaconic acids in the presence of platinum. 1 ml of each sample was dissolved in 50 ml of buffer. In other respects the conditions of polarographing were the same as in the preceding experiment (Table 13, Fig. 11). In the present case S = 0.935.

13. Hydrogenation of a mixture of itaconic and cinnamic acids in the presence of palladium. For analysis, 1 ml of each sample was dissolved in 25 ml of 0.1 N HCl in 50% ethanol. Under these conditions itaconic acid polarographed, but cinnamic acid did not (Table 14, Fig. 12). S = 0.860.

From an analysis of the experiments cited we first of all are convinced that the hypothesis proposed by Lebedev, that mixtures of ethylene derivatives of one degree of substitution are hydrogenated simultaneously, i.e., in other words, non-selectively, cannot be considered as a general principle. The nature of the saturation of binary mixtures, the degree of selectivity of saturation, fluctuates (depending on the nature of the components of the mixture and the nature of the catalyst) within wide limits – from 0 to 1. Thus, for example, in experiments which we carried out with a palladium catalyst, we found on the one hand, such pairs as maleic and cinnamic acids, or fumaric and oleic acids, which hydrogenated together at almost the same rates, and, on the other hand, such pairs as maleic and oleic acids (S = 0.97) or fumaric and cinnamic acids (S = 0.92) where one component did not react until the second was almost completely hydrogenated. Finally, we observed cases of not strictly expressed selectivity, when two components of a mixture hydrogenated simultaneously, but with sharp differences of rates; such, for example, occurs in a mixture of cinnamic and oleic acids (S = 0.81).

In the experiments with a platinum catalyst not one of the number of binary mixtures of symmetrically disubstituted ethylenes which we studied presented a picture of completely non-selective hydrogenation. Here individual pairs showed complete selectivity in the process of saturation, as, for example, maleic and cinnamic (S = 0.99) and fumaric and cinnamic acids; others showed a great or slight degree of deviation from absolute selectivity, as, for example, mixtures of cinnamic and oleic (S = 0.83) and maleic and oleic (S = 0.61) acids.

Concerning mixtures of symmetrical and asymmetrical (itaconic acid) disubstituted ethylenes, here there was always observed a more or less clear selectivity in operations with both palladium and platinum, in which in all cases the symmetrically disubstituted ethylene hydrogenated first.

SUMMARY

If all the disubstituted ethylene derivatives studied are arranged in a series, the selective designated by the symbol > and the non-selective saturations designated by the symbol =, then for the hydrogenation with palladium the series, maleic acid = cinnamic acid > oleic acid = fumaric acid > itaconic acid is obtained, and for hydrogenation with platinum the series, maleic acid > fumaric acid > cinnamic acid > oleic acid > itaconic acid, is obtained.

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Received November 2, 1953

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GRIGNARD-WÜRTZ REACTIONS WITH β- AND γ-ALKYNYL HALIDES

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In a number of instances it has been shown by different investigators [1-3] that condensation of allyl types of halides with both tertiary and primary alkylmagnesium halides proceeds with high yields, and may serve as a convenient method for the synthesis of various olefins, and also – as a result of hydrogenation – the paraffin hydrocarbons. The reaction, of course, considering the allyl rearrangement mechanism, can also be used for allyl type halides which are capable of isomerizing, but here it is necessary to carry out the reaction in a larger volume, keeping in mind the fractionation for the purposes of removal of the isomer which is present as an admixture, and the lowered yields of the branched halides [4].

Whereas the introduction of a multiple bond in the β-position makes the halide considerably more active, compared with the alkyl halide of the same structure, and in a number of cases (for branched halides) enables us also to carry out reactions which do not occur at all in the absence of a multiple bond, the presence of a double bond in the α- and γ-positions, on the other hand, reduces the activity of the halides almost to zero [5]. Likewise, both tertiary and secondary and primary halides with a double bond in the γ-position were shown to be inactive. There are some investigations in the literature devoted exclusively to the condensation reaction of alkynylmagnesium halides with tertiary alkynyl halides with a triple bond in the β-position [6]. In these investigations were noted both the high yield specified by the triple bond, and also the presence of acetylene-allene-diene rearrangements, the extent of which depends on the nature of the halohydrin of the acetylene alcohol and on the nature of the Grignard reagent.

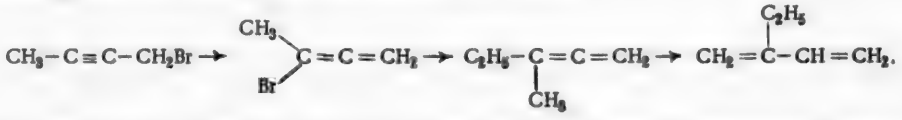
The study of the behavior in condensation reactions of primary alkynyl halides with a triple bond in both the β- and γ-positions was the problem of the present work. We planned for investigation the condensation of

C_2H_5MgBr with $CH_3-C\equiv C-CH_2Br$ (I) and with $CH_3-C\equiv C-CH_2-CH_2Br$. (II)

We were able to obtain the first bromide relatively easily. In the synthesis of the alcohol corresponding to the second halide, according to Iotsich's method [7], ethylenebromohydrin, which was characterized by the same boiling point and d_4^{20} 1.7720, was obtained instead of the alcohol. Apparently, this alcohol was not obtained by Iotsich either, who for its characteristics was limited to the citation of its boiling point. We were able to obtain this alcohol, having d_4^{20} 0.9002, by condensation of ethylene oxide with Na-methylacetylene, but for study of the Grignard-Würtz reaction we preferred to use the more readily available bromohydrin of its analog $C_4H_9-C\equiv C-CH_2-CH_2Br$ (III). As also with its olefin analog, condensation of the halide (III) with C_2H_5MgBr did not take place at all. The condensation of the halide (I) went according to the scheme:

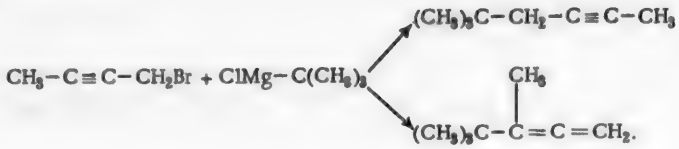
$$\underset{(I)}{CH_3-C\equiv C-CH_2Br} + C_2H_5MgBr \rightarrow CH_3-C\equiv C-CH_2-C_2H_5 + CH_3-C\equiv C-CH_2-CH_2-C\equiv C-CH_3.$$

The smaller yield of the acetylene hydrocarbon (25%) instead of the 50% yield noted in the condensation of the tertiary acetylenyl halide, and the formation of octadiyne-2,6 was characteristic of the reactions. All this indicates the lower rate of condensation of the primary acetylene β-halide compared with the tertiary. We were unable to detect an allene-diene rearrangement here; however, it is possible that it occurred partially, but that the isoprene homolog which formed was converted to a resinous polymer.



Favoring this conclusion also is the circumstance that the condensation reaction of this alkynyl halide with $(CH_3)_3CMgBr$ and C_6H_5MgBr took place with a yield of the C_8H_{14} and $C_{10}H_{10}$ hydrocarbons not exceeding 10% (all the rest produced resinous polymers), a spectrographic analysis of these hydrocarbons showed that they, in addition to triple bonds, contained conjugated double bonds. This latter circumstance induced us to repeat the synthesis and to carry out an ozonization of the synthesis products, which showed that the reaction proceeds here

according to the scheme:



EXPERIMENTAL

1. Reaction of 1-bromobutyne-2 (I) with C_2H_5MgBr. Butyn-2-ol-1 was obtained from 1,3-dichlorobutene-2 by saponification, according to Tishchenko [8], followed by the splitting off of HCl, according to Mkryan [9]; 1-bromobutyne-2 was obtained under the conditions of [10]. 3 g of dry pyridine was added to 50 g of butyn-2-ol-1 dissolved in 150 ml of dry ether, and 80 g of PBr_3 in 40 ml of ether was added dropwise. 48 g (50%) of 1-bromobutyne-2 was obtained:

B.p. 40-41° at 19mm, n_D^{20} 1.5090, d_4^{20} 1.5191, MR_D 26.12, calc. 26.36.
Found %: C 36.08, 35.82; H 3.35, 3.49; Br 60.57, 60.85. C_4H_5Br. Calculated %: C 36.09; H 3.7; Br 60.05.

30 g of 1-bromobutyne-2 in 50 ml of ether was added dropwise to ethylmagnesium bromide, prepared from 7 g of magnesium, 30 g of C_2H_5Br and 100 ml of ether. A strong evolution of heat was observed on addition of the acetylene bromide. After a 4-hour stirring at the boiling point of ether, the product was decomposed, washed and dried. 2 fractions were obtained: 1st, 79-85°, 5 g (25%); 2nd, 80-85° at 45 mm, 8 g; and a residue of 3 g, a resinous product.

The 1st fraction was hexyne-2: n_D^{20} 1.4121, d_4^{20} 0.7465. The Raman* spectrum showed the presence of the frequencies 2240, 2234 and 2303 cm^{-1}, which corresponded to hexyne-2. By hydration a ketone was obtained, the semicarbazone of which melted at 120°, which corresponded to the melting point of the semicarbazone of methyl butyl ketone.

The 2nd fraction was octadiyne-2,6:

n_D^{20} 1.4740, d_4^{20} 0.8414, MR_D 35.40; calc. 35.01.
Literature values [11]: B.p. 62° at 19 mm, n_D^{30} 0.828, d_4^{30} 1.4658.

The absorption spectrum in the infrared region showed the presence of the following bands (up to 7 μ): 3.4, 4.58 and 6.07 μ. On the basis of the fact that the band corresponding to the C≡C bond had a large intensity, it followed that the C≡C bond was not located in the middle of the molecule.

On conducting of an experiment in the reverse order, i.e., by addition of ethyl bromide to the butynylmagnesium bromide, no C_6H_{10} fraction, but only octadiyne-2,6, formed. By the Raman method the latter showed the presence of both triple and double bonds.

2. Reaction of 1-bromobutyne-2 (I) with tert.-C_4H_9MgCl. 50 g of 1-bromobutyne-2 was added to tert.-C_4H_9MgCl, prepared from 12 g of magnesium and 55 g of tert.-C_4H_9Cl in 200 ml of ether. A violent boiling was observed on addition of the C_4H_5Br. The reaction was carried out under the same conditions as was the preceding synthesis. 5 g (10%) of the hydrocarbon was obtained:

B.p. 38-42° at 25 mm, n_D^{20} 1.4302, d_4^{20} 0.7923 and a resinous product.
Found %: C 86.52, 86.11; H 11.82, 11.93. C_8H_{14}. Calculated %: C 87.26; H 12.73.

The taking of a Raman spectrum showed the presence of the frequencies 2236(4), 2299(5), 3060, 1605 (b), 1638(5), 1026(5), which indicated the presence of compounds with double and triple bonds.

4.5 g of the hydrocarbon was ozonized. Among the acid ozonization products we were able to identify formic acid by the calomel method, and acetic acid by the cacodyl test. The tert.-butylacetic acid was lost. In order to demonstrate the presence of oxalic acid, the sodium salts of the acids were converted to the calcium salts. The calcium salt of oxalic acid was separated from the salts of the other acids and decomposed with 10% H_2SO_4; the oxalic acid was extracted with ether. After evaporation of the ether, and recrystallization from water, oxalic acid with a m. p. of 99° was separated. Pinacoline, from the neutral products, was identified as the 2,4-dinitrophenylhydrazone with a m. p. of 124°. An addition product with maleic anhydride was obtained, which we were unable to

* Combination light scattering.

separate in pure form by recrystallization. Thus, the resulting hydrocarbon was a mixture of acetylene, allene, and possibly diene hydrocarbons.

3. Reaction of 1-bromobutyne-2 (I) with C_6H_5MgBr. 45 g of 1-bromobutyne-2 was added dropwise to phenylmagnesium bromide, prepared from 11 g of Mg, 150 ml of ether and 60 g of C_6H_5Br. The reaction was carried out under conditions similar to those of the first synthesis. 10 g of the original acetylene bromide and 12 g of the hydrocarbon with a b.p. of 70-82° at 13 mm were obtained:

n_D^{20} 1.5346, d_4^{20} 0.9658, MR_D 41.89; calc. 42.76.
Found %: C 91.52, 91.81; H 7.62, 7.58; $C_{10}H_{10}$. Calculated %: C 92.30; H 7.72.

Investigation of the resulting compounds by the Raman method showed the presence of the following frequencies: 186(1), 619(4), 812(2), 922(2), 1002(8), 1027(5), 1605 (5b), 1638(3), 2237(5), 2294(4) and 3060(5), which indicated the presence of a monosubstituted aromatic ring, and a double and triple bond in the molecules. We were unable to obtain the addition compound with maleic anhydride; a resin separated.

4. Reaction of 1-bromoctyne-3 (III) with RMgX. Octyn-3-ol-1 was prepared by method [12] from sodium hexynide and ethylene oxide in liquid ammonia. The yield was 40% based on the hexyne which reacted. The b.p. was 106° at 92 mm, n_D^{20} 1.4540. The 3,5-dinitrobenzoate of octyn-3-ol-1 had a m. p. of 45°.

Found %: N 8.85, 8.87. $C_{15}H_{16}O_6N_2$. Calculated %: N 8.75.

1-Bromoctyne-3 was obtained under the conditions specified in the literature [10]. 20 g (55%) of 1-bromoctyne-3 was obtained from 25 g of octyn-3-ol-1 in ether and pyridine, and 25 g of PBr_3:

B. p. 90-93° at 22 mm, n_D^{20} 1.4650, d_4^{20} 1.1387, MR_D 45.66; calc. 44.84.
Found %: Br 40.82, 41.42. $C_8H_{13}Br$. Calculated %: Br 42.32.

40 g of 1-bromoctyne-3 was added to ethylmagnesium bromide, prepared from 6 g of magnesium and 38 g of C_2H_5Br in 150 ml of ether. No evolution of heat from the reaction substance was observed. The temperature of the reaction substance was brought to 35°, and the mixture was boiled for 12 hours, after which the product was treated by the usual method. The original acetylene bromide was recovered.

5. Preparation of the Grignard reagent from 1-bromobutyne-3. By preparation of the original product of butyn-3-ol-1 by method [12], we obtained, together with the alcohol, the 3-butynoic ether of ethylene glycol (not mentioned in [12]). 30 g (42%) of butyn-3-ol-1 and 5 g of the 3-butynoic ether of ethylene glycol were obtained from 24 g of sodium, 700 ml of ammonia, acetylene, and 55 g of ethylene oxide. The 3,5-dinitrobenzoate of butyn-3-ol-1, m. p. 112°, was obtained with α-naphthylamine.

Found %: C 61.25, 60.98; H 4.38, 4.49. $C_{21}H_{17}O_6N_3$. Calculated %: C 61.90; H 4.17.

The 3-butynoic ether of ethylene glycol had:

B. p. 80° at 12 mm, n_D^{20} 1.4525, d_4^{20} 0.9939, MR_D 30.97; calc. 31.06.
Found %: C 63.38, 63.13; H 8.94, 9.03. $C_6H_{10}O_2$. Calculated %: C 63.15; H 8.85.

The substance gave a white precipitate with $AgNO_3$. The 3,5-dinitrobenzoate of the 3-butynoic ether of ethylene glycol had a m. p. of 52°.

Found %: C 50.75, 50.65; H 4.05, 4.15; N 9.85. $C_{13}H_{12}O_7N_2$. Calculated %: C 50.14; H 3.82; N 9.91.

The 3,5-dinitrobenzoate of the 3-butynoic ether of ethylene glycol with α-naphthylamine had a m. p. of 75°.

Found %: C 61.20, 61.40; H 4.64, 4.84. $C_{23}H_{21}O_7N_3$. Calculated %: C 60.81; H 4.65.

Depending on the order of addition of the reagents, we obtained the sulfite of butyn-3-ol-1 and 1-chlorobutyne-3.

The sulfite of butyn-3-ol-1. $(HC\equiv C-CH_2-CH_2O)_2SO$. 35 g of thionyl chloride was added dropwise during 1 hour to 10 g of butyn-3-ol-1, 30 g of pyridine, and 30 ml of dry ether at 0°. After addition of the $SOCl_2$ the temperature was brought to room temperature, and stirring was continued for 3 hours, after which ice water at 0° was added. The product was extracted with ether, neutralized with soda and dried with $CaCl_2$. 5 g (39%) of the sulfite was obtained.

B. p. 120° at 10 mm, n_D^{20} 1.4750, d_4^{20} 1.1341, MR_D 46.16; calc. 46.27.
Found %: S 17.28, 16.90; C 51.80, 51.87; H 5.52, 5.38. $C_8H_{10}O_3S$. Calculated %: S 17.20; C 51.61; H 5.30.

1-Chloro-butyne-3 was obtained by a reverse addition of the reagents, i. e., the acetylene alcohol in pyridine was added to thionyl chloride dissolved in ether. From 16 g of butyn-3-ol-1 in 16 g of pyridine, and 35 g of thionyl chloride in 30 ml of ether, 8 g (38%) of 1-chloro-butyne-3 was obtained:

B. p. 33-34° at 25 mm, n_D^{20} 1.4402.
Literature values [13]: B. p. 86° at 762 mm, n_D^{20} 1.4382.

The 1-chloro-butyne-3 did not react with magnesium.

An organomagnesium compound was obtained from 2 g of magnesium and 20 g of bromo-1-butyne-3 by addition of $HgCl_2$ in ether. A current of CO_2 was passed into the organomagnesium compound. After the usual treatment, and after removal of the ether, 3 g of a resinous product remained in the flask. From the resinous product, by extraction with petroleum ether, white crystals of pentynoic acid $HC\equiv C-CH_2-CH_2-COOH$ with a m. p. of 53°, obtained earlier by another method (from the dibromide) [14], were separated.

Pentyn-3-ol-1 An attempt to obtaine pentyn-3-ol-1, according to Iotsich, from methylacetylenemagnesium bromide and ethylene oxide was unsuccessful. On carrying out the reaction at an increased temperature (38-40°), decomposition with evolution of a brown, corrosive smoke was observed. We were able to obtain pentyn-3-ol-1 only from sodium methylacetylenide and ethylene oxide in liquid ammonia. The yield was 23%;

B. p. 34° at 9 mm, n_D^{20} 1.4450, d_4^{20} 0.9002, MR_D 24.82; calc. 24.81.
Phenylurethan: acicular crystals with m. p. 77°.
Found %: N 6.91, 7.04. $C_{12}H_{13}O_2N$. Calculated %: N 6.89.
3,5-Dinitrobenzoate m. p. 86°.
Found %: C 52.30; H 3.98; N 10.10. $C_{12}H_{10}O_6N_2$. Calculated %: C 51.79; H 3.60; N 10.07.

The optical investigations were made by Yu. P. Egorov.

SUMMARY

1. It was shown that a mixture of acetylenic and dienic hydrocarbons is formed by reaction of a primary alkynyl halide, which contains the triple bond in the β-position, with RMgX [where R = C_2H_5, $(CH_3)C$, and C_6H_5].

2. It was shown that, similar to the halohydrins of the olefin series, a holohydrin which contains the triple bond is the γ-position did not condense with RMgX.

3. Pentyn-3-ol-1, its derivatives and a series of derivatives of other acetylenic alcohols were obtained for the first time.

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Received February 19, 1954

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CONTACT TRANSFORMATIONS OF PROPYLCYCLOHEPTANE IN THE PRESENCE OF PLATINIZED CARBON

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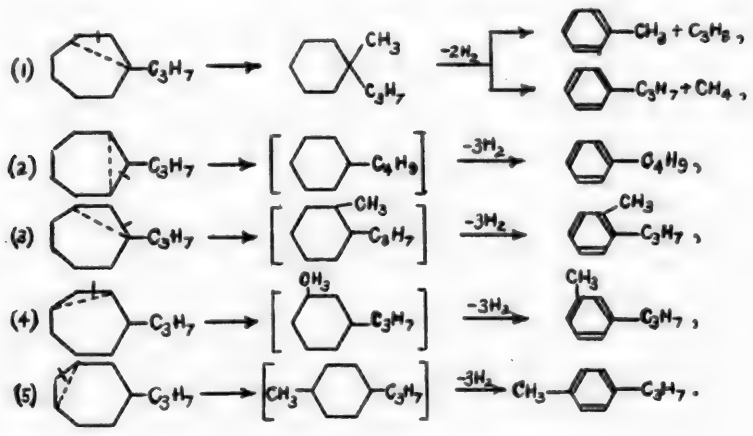
In previous investigations [1] we showed that, on passing the simplest alkyl- and arylcycloheptane hydrocarbons over platinized carbon under the conditions of dehydrogenation catalysis, isomerization of the seven-membered ring to a six-membered ring took place with the formation of considerable quantities of gem-dialkylsubstituted cyclohexane hydrocarbons. For example, methylcycloheptane contacted at 320° with platinized carbon, together with the formation of aromatic hydrocarbons (toluene, ethylbenzene, m-, p- and o-xylols), gave about 17% of gem-dimethylcyclohexane. Under similar experimental conditions ethylcycloheptane gave about 11% of gem-methylethylcyclohexane, and also a mixture of aromatic hydrocarbons consisting of ethylbenzene, and m-, o- and p-methylethylbenzenes. Phenylcycloheptane, under the same experimental conditions, gave about 7% gem-methylphenylcyclohexane and also a complex mixture of aromatic hydrocarbons.

It was of interest to study the phenomenon of contact isomerization of hydrocarbons of the cycloheptane series, which we observed, for propylcycloheptane. The propylcycloheptane which we synthesized was contacted with 10% activated carbon at 320°. The liquid portion of the catalyzate, in order to separate the naphthenic hydrocarbons from the aromatic hydrocarbons, was subjected to a chromatographic adsorption on silica gel. The naphthenic fraction, separated as a result of the chromatographic adsorption, consisted of gem-methylpropylcyclohexane. The aromatic fraction obtained by chromatographic adsorption was distilled from a column having an efficiency of 40 theoretical plates. The composition of the aromatic hydrocarbon fraction was established both by chemical methods and by a study of the Raman spectra.

On the basis of the results of the investigation, the approximate proportion of hydrocarbons in the total catalyzate of the contact transformation of propylcycloheptane (in %) was as follows: gem-methylpropylcyclohexane about 28, propylbenzene about 30, o-methylpropylbenzene about 20, m-methylpropylbenzene about 9, p-methylpropylbenzene about 8, butylbenzene about 4, and toluene about 1.

The directions of the contact transformation reactions of propylcycloheptane, under the experimental conditions which we selected, were analogous to those of the transformations of the alkylcycloheptanes which we studied earlier, and can be expressed by the following reaction scheme:



The presence of propylbenzene and toluene in the contact transformation reaction products of propylcycloheptane, to a high degree of probability can be accounted for by the occurrence of a secondary process – the catalytic transformation of gem-methylpropylcyclohexane (1). Earlier we observed a similar phenomenon of catalytic cleavage of the methyl group, encountered in the gem-methylalkylcyclohexanes during a study of the behavior of these hydrocarbons in reactions over platinized carbon, under the conditions of dehydrogenation catalysis [2].

EXPERIMENTAL

Synthesis of Propylcycloheptane

1-Propylcycloheptanol-1 was obtained from suberone and propylmagnesium bromide. This alcohol was dehydrated in the presence of iodine, and moreover, the 1-propylcycloheptene-1 which was obtained was hydrogenated to propylcycloheptane over platinized carbon at room temperature. After a vacuum distillation the propylcycloheptane had the following constants:

B. p. 181.4° (750 mm), 61.0° (9 mm), n_D^{20} 1.4500, d_4^{20} 0.8178, MR_D 46.01; calc. 46.18.
6.445 mg sub.: 20.248 mg CO_2; 8.348 mg H_2O. 6.160 mg sub.: 19.320 mg CO_2; 7.950 mg H_2O.
Found %: C 85.74, 85.60; H 14.49, 14.44. $C_{10}H_{20}$. Calculated %: C 85.63; H 14.37.

The yield of propylcycloheptane was 31.6% of the theoretical, based on suberone.

Literature values [3]: B. p. 183-184° (756 mm), n_D^{18} 1.4502, d_4^{18} 0.8175.

Contact Transformations of Propylcycloheptane

60 ml of 10% platinized carbon was placed in a catalytic tube, and 35 g of propylcycloheptane was passed over the catalyst (without a gas-carrier) at 320° at a volume rate of 0.2.

The results of the experiments are cited in Table 1.

TABLE 1

Experiment No.	n_D^{20} of catalyzate	Quantity of gas evolved (in liters)	Weight of catalyzate obtained (in g)
1	1.4680	9.78	31.2
2	1.4770	4.55	30.3
3	1.4805	3.31	29.7
4	1.4840	3.15	29.5

The gaseous products of the catalysis were analyzed in a VTI apparatus. The results of the gas analysis (in %) were: H_2 90.3; C_nH_{2n+2} 9.1.

Investigation of the catalyzate. In order to separate the naphthenic hydrocarbons from the aromatic hydrocarbons which formed during catalysis, the catalyzate obtained by the contact transformations of propylcycloheptane was subjected to a chromatographic adsorption on silica gel. The naphthenic fraction (8.5 g) isolated by this method of separation boiled at 172-174° (757 mm) and had n_D^{20} 1.4888, d_4^{20} 0.8089. A comparison of the constants of the resulting fraction with those of the gem-methylpropylcyclohexane which we synthesized earlier [4], enabled us to assume that it consisted chiefly of gem-methylpropylcyclohexane. The constants of the gem-methylpropylcyclohexane which we synthesized were as follows: b. p. 174.0-174.5° (759 mm), n_D^{20} 1.4445, d_4^{20} 0.8077.

TABLE 2

Fractions	Boiling range (in ° at 752 mm)	n_D^{20}	d_4^{20}	Weight of fraction	Content of fractions (in wt. %)
1	110 - 115	1.4967	–	0.2	1.0
2	115 - 156	1.4930	–	0.5	2.4
3	156 - 160	1.4921	0.8625	7.5	36.8
4	160 - 181	1.4956	0.8652	0.6	2.9
Residue		–	–	10.5	51.5
Losses		–	–	1.1	5.4

The aromatic fraction, separated by chromatographic adsorption on silica gel, was distilled.

The results of the distillation are presented in Table 2.

On distillation of the residue (10.5 g) from a small flask, a 5th fraction, which boiled in the range of 181-185° (758 mm), n_D^{20} 1.5011, d_4^{20} 0.8713, was obtained in a quantity of 10.3 g. We used both a chemical method of investigation, and the Raman method of investigation, in order to establish the composition of the individual fractions of the catalyzate of propylcycloheptane.

a) Optical investigation of the catalyzate. Literature values for the spectrum of n-propylbenzene [5], and for the isomeric o-, m- and p-methylpropylbenzenes [6], and also for the spectrum of gem-methylpropylcyclohexane, which we studied earlier [4], were used for interpretation of the Raman spectra of the catalyzate. The dearomatized portion of the catalyzate, and also the 3rd fraction and 5th fraction (obtained by fractionation of the residue) of the aromatic portion of the catalyzate, was subjected to an optical investigation.

The spectrum of the dearomatized portion of the catalyzate was shown to be identical with that of gem-methylpropylcyclohexane. The presence of propylcycloheptane in it was not detected.

The 3rd fraction (b. p. 156-160°) of the aromatic portion of the catalyzate contained chiefly propylbenzene, which was identified by a complete set of frequencies.

The 5th fraction (b.p. 181-184°) contained 1-methyl-2-propylbenzene, 1-methyl-3-propylbenzene and 1-methyl-4-propylbenzene, the presence of which was established by a set of analytically significant frequencies.

Using data on the line intensities in the spectra of the individual hydrocarbons [6] and data on the blackening of the analytical lines in the spectrum of the fraction, we were able to make an approximate determination of the quantitative composition of the 5th fraction. Calculation showed that it had the following composition (in %): 1-methyl-2-propylbenzene about 48, 1-methyl-3-propylbenzene about 25, 1-methyl-4-propylbenzene about 22.

Moreover, in the 5th fraction, obviously butylbenzene was present (there were lines of this hydrocarbon superimposed with lines of the other components of the fraction; however, there was also a non-superimposed line of 621 cm^{-1}, which most likely belonged to butylbenzene).

b) Chemical investigation of the catalyzate. The 1st fraction (b. p. 110-115°), as its constants showed, consisted chiefly of toluene. On nitration of this fraction, a nitro product was obtained which after recrystallization from ethanol had a m. p. of 69-70°. A test of a mixture with 2,4-dinitrotoluene gave no melting point depression.

The 2nd fraction (b. p. 115-156°), because of its wide boiling range and because of its small quantity, was not studied.

TABLE 3

Fractions	Boiling range at 752 mm	Quantity		Per cent content					
		(in g)	in percentages of total quantity of aromatics	toluene	propylbenzene	methylpropylbenzene ortho	methylpropylbenzene meta	methylpropylbenzene para	butylbenzene
1	110 - 115°	0.2	1.0	1.0	–	–	–	–	–
2	115 - 156•	0.5	2.6	0.6	2.0	–	–	–	–
3	156 - 160	7.5	39.3	–	39.3	–	–	–	–
4	160 - 181	0.6	3.1	–	0.3	1.3	0.7	0.5	0.3
5	181 - 185	10.3	54.0	–	–	25.6	11.7	10.8	5.3
		19.1	100.0	1.6	41.6	27.5	12.4	11.3	5.6

• The approximate quantitative content of hydrocarbons in the 2nd fraction was calculated on the basis of the indices of refraction of the fraction studied and those of pure toluene and propylbenzene.

The 3rd fraction (b. p. 156-160°). 2 g of the fraction was oxidized by an aqueous solution of potassium permanganate [7]. 1.88 g of a solid acid, which after recrystallization and sublimation melted at 120°, was obtained as a result of the oxidation. A test of a mixture with pure benzoic acid showed no depression. On the basis of a comparison of the constants of the 3rd fraction with the literature values of the constants of propylbenzene and with the results of the oxidation, it could be assumed that it was chiefly propylbenzene.

The literature values for propylbenzene [5] are: b.p. 159.2° (751 mm), n_D^{20} 1.4919, d_4^{20} 0.8626.

The 4th fraction (b. p. 160-181°). In the oxidation products of 0.6 g of the fraction the following acids were obtained: benzoic (0.05 g), orthophthalic (0.13 g), isophthalic (0.08 g), and terephthalic (0.05 g). The formation of the acids could be attributed to the oxidation of propylbenzene, and o-, m- and p-methylpropylbenzenes.

The 5th fraction (b. p. 181-185°). On oxidation of 5.0 g of the fraction, the following acids were separated: benzoic (0.18 g), orthophthalic (1.21 g), isophthalic (0.53 g), and terephthalic (0.50 g).

The presence of benzoic acid in the oxidation products of the 5th fraction is accounted for, apparently, by the oxidation of butylbenzene, but not propylbenzene, since the boiling point of the latter (159.2°) is low for the boiling range of the 5th fraction. The formation of the phthalic acids should be attributed to the oxidation of o-, m- and p-methylpropylbenzenes.

The composition of the fractions was calculated (Table 3) on the basis of the physical constants of the individual fractions obtained by fractionation of the aromatic portion of the catalyzate of propylcycloheptane, and on the basis of the chemical investigation which we employed.

SUMMARY

The contact transformations of propylcycloheptane, in the presence of platinized carbon at 320°, was studied, and it was found that the transformations take place with the formation of considerable quantities of 1-methyl-1-propylcyclohexane and a mixture of aromatic hydrocarbons, consisting of toluene, propylbenzene, butylbenzene, o-, m- and p-methylpropylbenzenes.

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Received March 6, 1954

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CATALYTIC PRODUCTION OF MIXED KETONES FROM PRIMARY ALCOHOLS

III. KETONIZATION OF A MIXTURE OF n-BUTYL AND ISOAMYL ALCOHOLS

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Processes of the formation of mixed ketones by passing mixtures of primary alcohols, ethyl and n-butyl and ethyl and isoamyl, over a copper activated catalyst were described in previous reports [1, 2]. Further investigations provided a new confirmation of the applicability of these processes to other systems. Unlike the two systems studied, a mixture of butyl and isoamyl alcohols is characterized by an increase of the molecular weights of the alcohols and by the absence of ethyl alcohol, which, as already mentioned, itself has the capacity to form mixed ketones and acetone. As will be obvious below, propyl isobutyl ketone, in a yield of 25-30% of the theoretical, was obtained by ketonization of a mixture of butyl and isoamyl alcohols.

It can be concluded from an examination of the results of experiments with mixtures of butyl and isoamyl alcohols, in molar ratios of 1 : 1, 1 : 2, 2 : 1 and 3 : 1, at temperatures from 275 to 425°, and at a constant volume rate (150), that the highest yields of propyl isobutyl ketone are obtained at a temperature of 350-375° (Table 1). The optimum ratios of alcohols in the mixture proved to be the molar ratios of 2 : 1 and 3 : 1. The ester yields, reaching a maximum at 275-300°, decreased continuously with a further increase of the temperature.

TABLE 1

Temperature of experiments	Yields of products (in % of the original mixture of alcohols)						
	dipropyl ketone	propyl isobutyl ketone	diisobutyl ketone	aldehydes	esters	butyl alcohol	isoamyl alcohol
Molar ratio 1 : 1							
275°	0.6	0.6	1.2	7.2	54.5	9.0	18.9
300	1.6	1.2	1.6	7.3	50.8	7.2	14.1
325	5.0	4.8	1.0	13.1	37.5	5.7	5.6
350	6.3	6.2	2.4	14.3	23.6	2.3	7.4
375	6.4	8.4	3.9	25.0	19.0	3.4	6.3
400	4.5	6.7	1.4	24.2	7.3	3.5	17.0
425	3.4	7.4	5.0	9.7	6.6	5.6	12.8
Molar ratio 1 : 2							
275	0.0	1.9	0.0	3.0	41.6	6.9	24.8
300	0.0	2.7	0.0	5.8	50.5	6.2	18.0
325	1.1	4.3	0.0	6.4	45.5	3.5	14.5
350	10.8	0.9	0.0	18.0	30.5	5.3	8.0
375	4.0	7.9	2.0	17.0	16.2	2.0	7.5
400	13.1	5.1	5.1	9.9	11.9	1.5	6.2
425	0.9	2.3	27.0	12.7	11.8	4.3	10.7
Molar ratio 2 : 1							
275	0.2	2.3	0.0	3.2	46.6	22.5	14.0
300	4.3	2.7	0.0	11.0	58.1	12.2	10.5
325	5.3	5.1	3.0	10.2	45.9	8.0	1.8
350	8.5	10.4	5.3	10.9	36.0	7.9	0.0
375	13.7	8.4	2.4	10.8	17.8	8.8	0.0
400	3.8	9.5	4.0	18.5	12.1	15.2	0.0
425	4.4	8.7	1.5	12.6	9.7	18.0	11.4
Molar ratio 3 : 1							
350	26.6	3.6	0.0	8.4	11.2	2.8	5.6
375	22.0	15.6	2.6	10.2	7.3	0.0	4.0

At 350-375° a maximum was approached for mixed and symmetrical ketones.

Unlike the preceding systems, the aldehydes had a maximum at 375-400°, i. e., close to the maximum for ketones. The ester yields at the temperatures optimum for ketonization were always large (about 36%). In this case, apparently, the stage of ketonic decomposition of esters is the inhibiting stage in the formation of ketones. At high temperatures (375-400°) the decomposition of esters with the formation of aldehydes is likely. Also unlike the preceding systems, considerable quantities of a symmetrical ketone (dipropyl ketone) corresponding to the low-molecular alcohol, together with the mixed ketone, are formed during the ketonization.

TABLE 2

Volume rate	Yields of products (in % of the original mixture of alcohols)						
	dipropyl ketone	propyl-iso-butyl ketone	diisobutyl ketone	aldehydes	esters	butyl alcohol	isoamyl alcohol
52	24.9	5.0	3.5	6.0	10.2	6.0	8.3
100	33.5	10.2	1.0	5.2	4.3	3.2	4.7
150	22.0	15.6	2.6	10.2	7.3	0.0	4.0
202	2.3	2.9	0.6	16.2	13.7	26.2	15.8

TABLE 3

Experimental conditions	Yields of products (in % of original mixture of alcohols)					
	dipropyl ketone	propyl iso-butyl ketone	diisobutyl ketone	aldehydes	esters	butyl and iso-amyl alcohols
in the presence of hydrogen	22.0	15.6	2.6	10.2	7.3	4.0
without hydrogen (1st hour)	23.0	4.6	0.0	10.6	8.6	7.6
without hydrogen (2nd hour)	15.6	4.5	3.0	12.5	8.8	17.0

A study of the effect of volume rate was carried out under optimum conditions (molar ratio of mixture 3 : 1, temperature 375°). The volume rate was varied from 50 to 200. It is evident from the data of Table 2 that the yields of propyl isobutyl ketone increased with an increase of the volume rate from 50 to 150, but decreased sharply with a further increase to 200. Decrease of the contact time brought about an increase of the yields of aldehydes and esters. A comparison of the ketone yields, on the one hand, and that of the aldehydes and esters, on the other, serves to verify the hypothesis of the intermediate formation of aldehydes and esters during ketonization.

In order to study the effect of hydrogen, a mixture of alcohols in a molar ratio of 3 : 1 was passed over the catalyst at 375° without simultaneous passage of hydrogen. From the data of Table 3 it follows that in the absence of hydrogen the yields of propyl isobutyl ketone were sharply reduced, the yields of aldehydes and esters increased simultaneously, and the quantities of unreacted original alcohols increased.

We also investigated two mixtures with participation of methyl alcohol (methyl-ethyl, methyl and n-butyl alcohols). Experiments with the first mixture were carried out at alcohol molar ratios of 1 : 1 and 1 : 2 and at temperatures from 275 to 325°. Experiments with the second mixture were carried out at the same alcohol ratios and at temperatures from 275 to 375°. The experiments, a detailed description of which is not cited, showed that under the conditions indicated, partial or complete decomposition of the methyl alcohol to CO and H_2 occurs and low yields of the liquid products were obtained. No mixed ketones were formed. Thus, mixtures of methyl alcohol with other primary alcohols were unsuitable for carrying out the ketonization reaction (at least at ordinary pressure).

Examining schemes of consecutive transformations of primary alcohols to ketones which are known in the literature [1], with consideration of our experimental data obtained in the ketonization investigation of binary mixtures of primary alcohols, it should be noted that Klyukvin and Ipatyev's aldol mechanism proved to be inapplicable to this process. Neither aldols nor the corresponding secondary alcohols, assumed to be intermediate products of the aldol scheme, were found in a single instance in the reaction products.

The available facts indicated the use of the ester scheme of Sabatier-Kagan, Sobolev and Lyubarsky. Considerable quantities of esters were invariably observed in the reaction products at low temperatures. For a mixture of ethyl and isoamyl alcohols, all four of the esters the formation of which could be assumed by the ester scheme, the ethyl and isoamyl esters of isovaleric acid, the ethyl and isoamyl esters of acetic acid, were separated and identified. In experiments with other mixtures we were able to separate only some of the possible esters; however, the presence of

fractions corresponding in boiling point, and the analyses of these fractions showed that all the esters specified by the ester mechanism are always formed in some quantity.

The fact of the formation of four esters and three ketones for all the binary mixtures of primary alcohols was a strong argument in favor of the assumption that the mixed ketone, as well as two symmetrical ketones, is obtained through the intermediate formation of esters.

The ester yields depended on the experimental conditions: they decreased with an increase of temperature, and increased with an increase of volume rate, i.e., with a decrease of the contact time.

Aldehydes, like the esters, were always observed among the reaction products. Curves expressing the relationship of the aldehyde yields to the experimental temperature usually had minima at temperatures identical or close to the temperatures corresponding to the maxima for the mixed ketone. The aldehyde yields increased with a decrease of contact time.

Apparently, a complex equilibrium exists in the ketonization reactions of mixtures of primary alcohols:

$$RCHO + R'CHO \underset{> t^\circ}{\rightleftharpoons} RCOOCH_2R' \xrightarrow[> t^\circ]{} RCOR'.$$

With an increase of the temperature from 275 to 350°, a sharp decrease of the yields of the esters, and an increase of the yields of mixed ketones are observed. A further increase of the temperature led to a decrease of the yields of mixed ketones, and to an increase of the quantities of aldehydes, since with an increase of temperature the equilibrium is shifted toward the left, and dissociation of the esters with formation of aldehydes proceeds:

$$RCHO + R'CHO \underset{> t^\circ}{\rightleftharpoons} RCOOCH_2R'.$$

An increase of the volume rate decreased the yields of mixed ketones and produced an increase of the quantities of aldehydes, since the contact time became inadequate for occurrence of the condensation reaction of aldehydes and of the ketonic decomposition of the esters.

Supplementarily introduced hydrogen had a favorable effect on the ketonization reaction; it reduced the quantity of aldehydes and sharply increased the yield of mixed ketone. On the contrary, in the operation without additional hydrogen a considerable increase of the aldehyde yields, and a decrease of the yields of mixed ketones was observed, i.e., the stage of further aldehyde transformations – condensation to esters and ketonic decomposition of the latter – was inhibited. Moreover, the reduction of the yields of gaseous products which occurred, indicated a gradual lowering of the activity of the catalyst.

Some rules regarding the effect of the composition of the initial mixture of alcohols were established. The optimum temperature for formation of the mixed ketone was shifted toward an increase, in proportion to the increase of the molecular weight and the increase of branching of the initial alcohols. Thus, for the formation of methyl propyl ketone from a mixture of ethyl and butyl alcohols the optimum temperature was 325°, for the formation of methyl isobutyl ketone from a mixture of ethyl and isoamyl alcohols it was 350°, and for the production of propyl isobutyl ketone from a mixture of butyl and isoamyl alcohols it was 375°. The maximum yields of mixed ketones were obtained at molar ratios, between the alcohol with a lower molecular weight and the alcohol with the higher molecular weight, equal to 2 : 1. Predominance of the alcohol with the higher molecular weight in the mixture led chiefly to the production of the symmetrical ketone corresponding to this alcohol. On the contrary, an increase of the content of the alcohol with the lower molecular weight in the initial mixture to a ratio of 3 : 1 or 5 : 1 usually led to some decrease of the yields of mixed ketone and to an increase of the yields of the symmetrical ketone corresponding to the alcohol with the lower molecular weight.

The presence of carbon dioxide in the resulting gaseous products, apparently indicated the use of the ester mechanism of the process, although the presence of 8-10% CO and the too-small quantities of olefins (3-4%), compels us to refer to it with caution, the more so since CO_2 can be produced by the water gas reaction from the CO and water which formed during the condensation:

$$CO + H_2O \rightleftharpoons CO_2 + H_2,$$

where the quantities of CO_2 according to this reaction will be greater, the more thoroughly the condensation with formation of water proceeds, which was established by Bocharova and Dolgov [3]. In such a case the possibility of the occurrence of the process (possibly parallel) according to the Klyukvin-Ipatyev aldol scheme is not excluded, in favor of which is the small formation of olefins which, according to the ester scheme, should be obtained in an equimolar ratio to CO_2. The possibility of polymerization of the olefins was not excluded, especially since the

high-boiling residue which we did not investigate amounted to 5-15% of the initial mixture.

Considering the complexity of the process of the transformation of primary alcohols to ketones, we nevertheless, possibly only temporarily, adhered to the ester mechanism of Sabatier-Kagan: alcohols → aldehydes → esters → ketones.

For example, the formation of methyl propyl ketone from a mixture of ethyl and n-butyl alcohols proceeds according to the scheme:

$$2C_2H_5OH \rightarrow 2CH_3CHO + 2H_2;$$
$$C_4H_9OH \rightarrow 2C_3H_7CHO + 2H_2;$$
$$2CH_3CHO \rightarrow CH_3COOC_2H_5;$$
$$2C_3H_7CHO \rightarrow C_3H_7COOC_4H_9;$$
$$CH_3COOC_2H_5 + C_3H_7COOC_4H_9 \rightarrow CH_3COC_3H_7 + CO_2 + C_2H_4 + C_4H_9OH.$$

The overall reaction is:

$$2C_2H_5OH + C_4H_9OH \rightarrow CH_3COC_3H_7 + CO_2 + C_2H_4 + 4H2.$$

The formation of a mixed ketone from a mixture of two primary alcohols may be represented in general form by the scheme:

$$2R'CH_2CH_2OH + R''CH_2CH_2OH \rightarrow R'CH_2COCH_2R'' + CO_2 + R'CH=CH_2 + 4H_2 (R' < R'').$$

Parallel reactions lead to the formation of symmetrical ketones, for example:

$$2CH_3COOC_2H_5 \rightarrow CH_3COCH_3 + CO_2 + C_2H_4 + C_2H_5OH,$$
$$2C_3H_7COOC_4H_9 \rightarrow C_3H_7COC_3H_7 + CO_2 + C_4H_8 + C_4H_9OH, \text{ etc.}$$

The majority of the intermediate and final products produced, which were specified by the present schemes, were separated and identified. Judging by the presence of the corresponding fractions and by the analysis of the fractions, the substances which we were unable to isolate because of analytical difficulties, were all apparently present in the reaction products.

Considering the extreme complexity of the process, and the possibility of the simultaneous occurrence of a large number of side reactions and secondary reactions, it was impossible to consider the scheme which we postulated as exhaustive. According to the experimental data obtained, they were only first approximations to a path to the complete discovery of the mechanism of the process.

EXPERIMENTAL

n-Butyl alcohol, which after drying over Na_2SO_4 and after distillation had a b. p. of 116.5-118.0°, d^{18} 0.806, and n_D^{18} 1.3997, and isoamyl alcohol, which after drying over Na_2SO_4 and after distillation had a b. p. of 130.5-132.0°, d^{18} 0.816 and n_D^{18} 1.4080, were used for carrying out the work. The experiments were carried out in the same apparatus which was used for ketonization of the previous mixtures [1, 2].

The liquid condensates from each experiment were fractionally distilled. The following fractions were obtained by the distillations: 1st 65-80°, 2nd 80-100°, 3rd 100-120°, 4th 120-132°, 5th 132-140°, 6th 140-146°, 7th 152-158°, 8th 160-170°, and 9th 170-199°; and the residue (above 199°). The fractions from all the experiments which were identical in boiling point, after analysis for ketones, aldehydes, and esters, were combined and fractionated once more for the purpose of separation of the individual substances and their identification.

1st Fraction. On redistillation a fraction corresponding to butyraldehyde was separated:

B. p. 73.5-74.5°, d_4^{20} 0.8176, n_D^{20} 1.3844.
Literature values: b. p. 74.7°; d_4^{20} 0.8170, n_D^{20} 1.38433.
2,4-Dinitrophenylhydrazone: m. p. 126.0-126.3° (according to literature data 126.0°).
Found %: N 22.40. $C_{10}H_{12}O_4N_4$. Calculated %: N 22.22.

The 2nd fraction was a mixture of butyraldehyde and isovaleraldehyde and water. On redistillation with other fractions, an isovaleraldehyde fraction was separated:

B. p. 91.5-92.5°, d_4^{20} 0.7899, n_D^{20} 1.3923.
Literature values: b. p. 92.5°, d_{20}^{20} 0.7845, n_D^{20} 1.39225.
2,4-Dinitrophenylhydrazone: m. p. 122.0-122.5° (according to literature data 123°).
Found %: N 21.19. $C_{11}H_{14}O_4N_4$. Calculated %: N 21.05.

The 3rd, 4th and 5th fractions contained the unreacted original alcohols, butyl (100-120°) and isoamyl (120-132° and 132-140°).

The 6th fraction contained dipropyl ketone, which was isolated and identified:

B. p. 143.5-144.5°, d_4^{20} 0.8175, n_D^{20} 1.4069.
Literature values: b. p. 144.1°, d_4^{20} 0.8175, n_D^{22} 1.40732.
Found: M 112.7, 113.7. $C_7H_{14}O$. Calculated: M 114. Semicarbazone after two recrystallizations had a m. p. of 133.5-134.0°, (according to literature data 133.0°).
Found %: N 24.51. $C_8H_{17}ON_3$. Calculated %: N 24.56.

The 7th fraction contained almost pure propyl isobutyl ketone, which was isolated by a second distillation, and had the constants:

B. p. 154-155°, d_4^{20} 0.8186, n_D^{20} 1.4106.
Literature data: b. p. 155° (750 mm), d_0^{22} 0.813.
Found: M 127.2, 129.8. $C_8H_{16}O$. Calculated: M 128.
The semicarbazone after three recrystallizations had a m. p. of 123.0-123.5° (according to literature data 123-124°).
Found %: N 22.91. $C_9H_{19}ON_3$. Calculated %: N 22.70.

The 8th fraction contained esters; according to the analytical data the butyl ester of butyric acid (b. p. 166.6°) was probably present. Moreover, this fraction contained a certain quantity of diisobutyl ketone (b. p. 168°), which was demonstrated by production of the 2,4-dinitrophenylhydrazone, which after recrystallization had a m. p. of 65-66° (66° according to the literature).

The 9th fraction consisted of esters. The closeness of the boiling point appeared to be the reason why, of the four esters the presence of which was extremely probable (butyl butyrate 166.6°, isoamyl butyrate 178.6°, butyl isovalerate 175.7°, and isoamyl isovalerate 190.4°), the first three were not isolated. On a second distillation we were able to obtain in only a small quantity a fraction which corresponded in constants to isoamyl isovalerate:

B. p. 188-190°, d_4^{20} 0.8572, n_D^{20} 1.4127.
Literature values: b. p. 190.4° $d_4^{18.7}$ 0.8583, $n_D^{18.7}$ 1.41300.

The residue (above 199°), according to analysis, contained esters and ketones; they were not studied further.

The composition of the gas from the experiments, the conditions of which were most favorable for production of the mixed ketone, was characterized by a considerable content of H_2 (80-83%) and CO (1-10%). It contained CO_2 in the quantity of 3-4%, olefins also 3-4%, but saturated hydrocarbons were absent.

SUMMARY

1. Molar ratios of n-butyl and isoamyl alcohols in the initial mixture, equal to 2 : 1 and 3 : 1, a temperature of 350-375°, and a volume rate of 100-150, were optimum conditions for the formation of propyl isobutyl ketone. The yields of propyl isobutyl ketone amounted to 15% of the initial mixture, dipropyl ketone about 22%, and diisobutyl ketone 2-3%. The total yield of ketones amounted to 40% of the initial mixture. At low temperatures (275-325°) esters were obtained in high yields (about 60%) of the initial mixture).

2. A general method of production of mixed ketones of the aliphatic series, including the passage of mixtures of primary alcohols over Dolgov and Bolotov's copper activated catalyst was proposed. The yields of the mixed ketones amounted to 20-25% of the initial mixture of alcohols (40-50% of the theoretical). The total yields of ketones, taking into account the formation of symmetrical ketones, amounted to 30-40% of the initial mixture (60-80% of the theoretical).

3. It was found that aldehydes and esters are intermediate products in the ketonization reaction of mixtures of primary alcohols over a copper activated catalyst.

4. Schemes of consecutive transformations of primary alcohols, known in the literature, were examined with consideration of the experimental data obtained. Results of the work essentially confirmed the validity of the Sabatier-Kagan ester mechanism. However, it is impossible to assume as completely excluded the possibility of a parallel occurrence of the process according to the Klyukvin-Ipatyev aldol scheme. Schemes of formation of mixed ketones from mixtures of primary alcohols were proposed.

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Received December 26, 1953

Leningrad State University

* T. p. = C. B. Translation pagination.

INVESTIGATIONS IN THE FIELD OF ASYMMETRICAL ORGANIC α-OXIDES

VIII. ISOMERIZATION OF THE ISOPROPYL ETHER OF GLYCIDOL AND ITS REACTION WITH AMMONIA

F. G. Ponomarev

In our previous works it was shown that the isopropyl ether of glycidol (I) adds amides of monobasic carboxylic acids [1] and diethylamine [2] with the formation of the corresponding nitrogenous derivatives of propanediol. The reaction of this ether of glycidol (I) with ethylenediamine was described somewhat earlier [3].

In the literature, other data relative to the transformations of this ether (I) are absent. In order to compare it with other asymmetrical α-oxides, it was of interest to study its behavior under the influence of different reagents.

The present report was devoted to an investigation of the transformations of the isopropyl ether of glycidol (I) under the action of aluminum oxide and zinc chloride, and also to the study of its reaction with ammonia. The experiments which we conducted showed that, under the influence of aluminum oxide and zinc chloride, the isopropyl ether of glycidol $CH_2-CH-CH_2OC_3H_7$-iso (I) isomerizes, according to the general scheme for monosubstituted ethylene oxide [4- 6], chiefly to β-isopropoxypropionaldehyde (II) and, possibly, to a slight extent to isopropoxyacetone (III).

$CH_2-CH-CH_2OC_3H_7$-iso; iso-$C_3H_7OCH_2-CH_2-CHO$; iso-$C_3H_7OCH_2-CO-CH_3$.
(I) (II) (III)

The structure of the resulting aldehyde (II) was demonstrated by its oxidation to β-isopropoxypropionic acid by a 1% solution of potassium permanganate. The β-isopropoxypropionic acid was identified as the silver salt.

With aqueous and alcoholic solutions of ammonia at room temperature the isopropyl ether of glycidol (I) forms the ether of aminopropanediol (IV), and possibly (V) and (VI):

$NH_2CH_2-CHOH-CH_2OC_3H_7$; $HN(CH_2-CHOH-CH_2OC_3H_7)_2$; $N(CH_2-CHOH-CH_2OC_3H_7)_3$.
(IV) (V) (VI)

The yield of the amino alcohol (IV) depends, as also from the reaction of ammonia with the methyl and ethyl ethers of glycidol, on the proportions of reagents [7]; but the isopropyl ether of glycidol reacts with ammonia somewhat more slowly since the reactivity of the ether oxides, as has already been recorded [8], decreases in a homologous series.

Formulas (IV-VI) for the resulting amino alcohols are assumed on the basis of the Krasusky law on the order of addition of ammonia to asymmetrical α-oxides [9].

The definite interest of this reaction resides in the fact that it discloses a possibility of synthesis by a relatively easy method of amino alcohols (IV) which are close to compounds of the $R-O-CH_2-CHOH-CH_2NR'R''$ type which as is evident from the literature, possess an anesthetizing action [10].

The primary amine (IV) was separated in sufficiently pure form, but the secondary and tertiary amines (V and VI) were obtained as a mixture and were not separated.

The diacetate (VII) of iso-$C_3H_7-O-CH_2-CH(OCOCH_3)-CH_2-NHCOCH_3$, was obtained by the acetylation of amino alcohol (IV) by acetic anhydride.

The isopropyl ether of aminopropanediol (IV) possesses basic properties; it forms crystalline salts – the picrate and oxalate. It forms no crystalline derivatives with auric chloride, ethyl iodide, hydrogen chloride and phosphoric acid.

EXPERIMENTAL

Isomerization of the isopropyl ether of glycidol (I) under the influence of aluminum oxide and zinc chloride (in collaboration with Yu. I. Kazakov).

a) 30 g of the isopropyl ether of glycidol was passed (at the rate of 10 g) at 300° over aluminum oxide, precalcined at the indicated temperature. The isomerization experiments were carried out in a glass tube with an internal diameter of 13 mm; the catalyst was taken as 60% of the weight of the ether oxide. The tube was heated by an electric furnace equipped with a thermoregulator. The ether of glycidol was supplied dropwise from a funnel at a rate of 10 g per 40-45 minutes.

After passage of each 10 g of the substance (I) a renewal of the catalyst was made, since it was poisoned, being covered with a layer of resinous substances. From 30 g of the ether oxide, 26.7 g (89%) of condensate was obtained as a yellowish liquid, with a pungent odor, which was highly soluble in alcohol and in ether, but difficultly soluble in water. On distillation of the condensate 9 g of the isomerizate (30% of the ether oxide taken) as a colorless liquid with a b. p. of 78-80°, and 12 g (40%) of the unaltered ether oxide with an extended b. p. of 130-135° owing to admixture of aldehyde (II) and ketone (III) in it, were collected.

Investigation of the isomerizate (b. p. 78-80°). It gave a crimson coloration with fuchsin sulfurous acid, and a red coloration with sodium nitroprusside. It formed a silver mirror with an ammoniacal solution of silver oxide.

Oxidation. 98 ml of a 1% solution of potassium permanganate was added in small portions, with stirring, to 1 g of the substance, and the mixture was heated on a water bath for 30 minutes until the pungent odor characteristic of aldehydes had dissappeared. The filtrate was treated with an ammonia solution. After removal of the excess of the latter by heating the mixture on the water bath in a porcelain dish, 24 ml of a 10% solution of $AgNO_3$ (25% excess) was added to the neutral solution of the ammonium salt of β-isopropoxypropionic acid which was cooled to room temperature. The silver salt which precipitated at once was filtered off, washed with water, dried to constant weight in a desiccator over P_2O_5 in the dark, and analyzed.

0.3609 g sub.: 0.1656 g Ag. Found %: Ag 45.90. $C_6H_{11}O_3Ag$. Calculated %: Ag 45.14.

b) 4 g of the isopropyl ether of glycidol and 0.4 g of fused zinc chloride were placed in a flask equipped with a mechanical stirrer and a reflux condenser, and the mixture was heated for 4 hours at a bath temperature of 125°. About 1 g of the above-described isomerizate (with a b. p. of 78-81°), and 3.3 g (83%) of the ether oxide which was polymerized, were obtained.

Reaction of the isopropyl ether of glycidol with ammonia. Synthesis of 3-isopropoxypropanol-2-amine (IV) (in collaboration with I. K. Getmansky).

The experiments were carried out by the usual method [7]. Their results are recorded in the table.

Experiments	Used in the reaction (in g)			Reaction conditions		Yield of amino alcohol based on ether oxide taken (in %)
	ether of glycidol (I)	ammonia		ratio of ether oxide to ammonia (in parts by weight)	time (in hours)	
		aqueous 25%	alcoholic 9%			
1	10.0	1000	–	1:100	72	63
2	23.2	696	–	1:30	72	54
3	11.6	175	–	1:15	72	48
4	11.6	116	–	1:1	72	10
5	70.0	–	1400	1:20	48	48
6	35.0	–	350	1:10	48	37
7	35.0	–	175	1:5	48	22

In all these experiments, after distillation of the product (IV) a residue remained in the flask. The residue, judging by the analytical data for nitrogen, was a mixture of substances (V) and (VI).

3-Isopropoxypropanol-2-amine (IV) had the following constants:

B. p. 97-99° at 100 mm, d_4^{20} 0.9884, n_D^{20} 1.4535, MR_D 36.49; calc. 36.50.

0.2081 g sub.; 15.56 ml 0.1 N H_2SO_4. 0.2322 g sub.; 17.18 ml 0.1 N H_2SO_4 (according to Kjeldahl). 0.1038 g sub.; 0.1806 g AgI. 0.1028 g sub.; 0.1796 g AgI (according to Zeisel). 0.1253 g sub.; 8.75 ml 0.1 N NaOH. 0.1145 g sub.; 8.02 ml 0.1 N NaOH [12]. 0.2034 g sub.; 28.15 g dioxane: Δt 0.30°. 0.1970 g sub.; 28.15 g dioxane: Δt 0.27°.

Found %: N 10.48, 10.37; C_3H_7O 43.93; OH 11.86, 11.90; M 128, 124. $C_6H_{15}O_2N$. Calculated %: N 10.52; C_3H_7O 44.46; OH 12.77; M 133.

3-Isopropoxypropanol-2-amine was a colorless liquid with a faint amine odor and a bitter, stinging taste. It had a great tendency toward supercooling, as a result of which it slowly (after a month) crystallized as colorless, acicular crystals which melted at 32°. We obtained this amino alcohol earlier, but it was characterized as a liquid [8]. It dissolved well in water, alcohol, and dioxane, but dissolved poorly in benzene; it did not dissolve in ether. It rapidly decolorized potassium permanganate and a chloroform solution of bromide. It gave characteristic reactions for the hydroxyl and primary amino groups (with metallic sodium, with sodium nitroprusside and acetone, with potassium hydroxide and chloroform) [11]. It was stable on long storage. Under ordinary conditions it absorbed CO_2 and H_2O from the air.

A weighed portion of 0.8660 g of the freshly-distilled substance, after 6, 24 and 36 hours, increased 16, 21 and 25% in weight, respectively.

The picrate of the amino alcohol, obtained by mixture of alcoholic solutions of equimolar quantities of product (IV) and picric acid, melted at 140-142° (from water).

0.0984 g sub.: 11.14 ml 0.1 N H_2SO_4. 0.1425 g sub.: 15.78 ml 0.1 N H_2SO_4 (according to Ekkert) [13]. Found %: N 15.86, 15.50. $C_{12}H_{15}O_9N_4$. Calculated %: N 15.45.

The oxalate of the base (IV) was obtained by heating solutions of the amino alcohol and oxalic acid (m. p. 189°) in anhydrous ether on the water bath for 2 hours, or in anhydrous toluene at 90° for 15 minutes. After two recrystallizations from anhydrous alcohol it melted at 148-149°.

0.1612 g sub.: 7.25 ml 0.1 N H_2SO_4. 0.1599 g sub.: 7.08 ml 0.1 N H_2SO_4 (according to Kjeldahl). Found %: N 6.29, 6.20. $C_8H_{17}O_6N$. Calculated %: N 6.27.

Acetylation of the amino alcohol (IV). The diacetate was obtained as a colorless, syrupy liquid by the action of freshly-distilled acetic anhydride (20% excess) on the amino alcohol:

B. p. 158-161° at 6 mm, d_4^{20} 1.0456, n_D^{20} 1.4491, MR_D 55.75; calc. 55.29.

0.1415 g sub.: 6.1 ml 0.1 N H_2SO_4. 0.2072 g sub.: 9.09 ml 0.1 N H_2SO_4 (according to Kjeldahl). 0.1426 g sub.: 1.297 ml 1 N KOH. Found %: N 6.04, 6.23; CH_3CO 39.13. $C_{10}H_{19}O_4N$. Calculated %: N 6.44; CH_3CO 39.63.

The diacetate dissolved well in ether, dioxane and benzene, contained no free hydroxyl groups, and gave no characteristic reactions for the primary amino group [11].

SUMMARY

1. The isomerization of the isopropyl ether of glycidol under the action of aluminum oxide and zinc chloride was studied.

It was shown that under the influence of these catalysts the ether oxide was isomerized chiefly to β-isopropoxypropionaldehyde, and possibly to a small extent to isopropoxyacetone.

2. The reaction of the isopropyl ether of glycidol with aqueous and alcoholic solutions of ammonia was studied.

The chief product of this reaction, 3-isopropoxypropanol-2-amine, was isolated and characterized. Its diacetate and some of its salts were described.

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Received December 22, 1953

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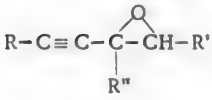
ISOMERIZATION OF α-OXIDES OF THE ACETYLENE AND VINYLACETYLENE SERIES

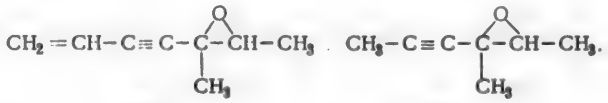
F. Ya. Perveev and N. I. Kudryashova

It was found earlier [1-5] that, by isomerization under the action of zinc chloride, α-oxides of the



type form an acetylenic aldehyde or ketone, depending on the structure of the initial oxide.

It was the purpose of the present work to study the isomeric transformations of oxides of the acetylene and vinylacetylene series, under the action of dilute sulfuric acid. 3-Methyl-epoxy-2,3-hepten-6-yne-4 (I) [6] and 3-methyl-epoxy-2,3-hexyne-4 (II) [7] were used for the investigation:



(I) (II)

A ketone, which was mobile and had the pungent odor of a liquid possessing lachrymatory properties, was formed by isomerization of 3-methyl-epoxy-2,3-hepten-6-yne-4 in acetic anhydride in the presence of a few drops of sulfuric acid. With semicarbazide it readily formed the semicarbazone. Even on long contact with an alcoholic solution of ferric chloride it gave no coloration. Its structure was demonstrated by oxidation. Methyl ethyl ketone and oxalic acid were among the oxidation products.

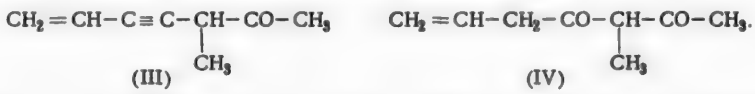
On the basis of the data obtained, we attributed the structure corresponding to the unsaturated ketone, 3-methyl-hepten-6-yne-4-one-2 (III), to the compound synthesized.

The methyl ethyl ketone formed as a result of the decarboxylation of the β-keto acid.

On isomerization of the same oxide by an aqueous solution of sulfuric acid, after repeated distillation two fractions were separated: 1st, b. p. 40° (3 mm); 2nd, b. p. 53-54° (1 mm).

According to its physical constants, the 1st fraction corresponded to 3-methyl-hepten-6-yne-4-one-2 (III). A test of a mixture of the semicarbazone with the semicarbazone obtained from substance (III) produced no melting point depression.

The 2nd fraction was a mobile liquid, which became yellow on standing, and gradually polymerized. It gave an intense violet coloration with an alcoholic solution of ferric chloride. Its elementary composition corresponded to the formula $C_8H_{12}O_2$. It could be assumed that we were dealing with the β-diketone (IV), which could be obtained by hydration of the triple bond in the presence of sulfuric acid:

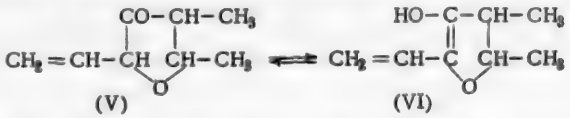


(III) (IV)

The substance was hydrogenated in methyl alcohol over Raney nickel in order to demonstrate its structure. Hydrogen was consumed in the quantity calculated for two double bonds. No further addition of hydrogen occurred. The hydrogenation product gave no coloration of enol with $FeCl_3$. It did not react with hydroxylamine and semicarbazide. The active hydrogen content, determined by the Terentyev-Shcherbakova method, corresponded to one hydroxyl group. The substance was not dehydrated (recovered unchanged) by heating with a 30% solution of sulfuric acid.

All the data cited indicated that the substance which we separated from the 2nd fraction was not the β-diketone. In addition, the isomerization product obtained with hydroxylamine gave an oxime, whereas the product of the reaction of the β-diketone with hydroxylamine is probably isooxazole. All this enabled us to assume that, together with the formation of the unsaturated ketone (III), tetrahydro-β-ketofuran (V), chiefly, with an admixture

of its enolic form (VI), was obtained on isomerization of the α-oxides with 30% sulfuric acid:

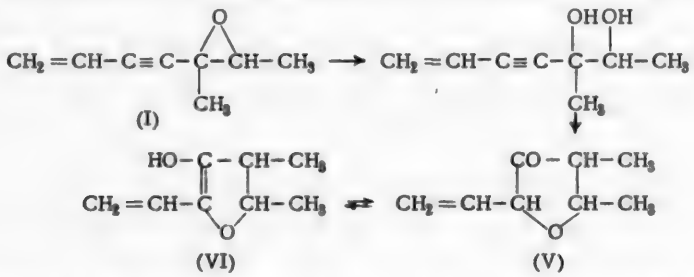


(V) (VI)

The per cent of the enolic form in the tautomeric mixture, determined by the Terentyev-Shcherbakova method, was equal to 53.8.

By the ozonization method it was demonstrated that there is a double bond in the side chain (quantity of formaldehyde determined was 47%). The capacity of the tetrahydro-β-ketofurans for enolization was first established by Dupont [8].

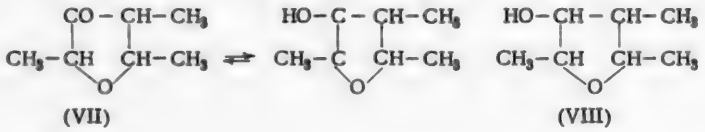
Apparently, the formation of the vinylalkyltetrahydro-β-ketofurans proceeds as follows:



(I) (VI) (V)

The easy mobility of the hydroxyl situated in the α-position to the triple bond was recorded in Nazarov's works [9] on the syntheses and transformations of divinyl ketones. A similar transformation confirmed the fact that, on treatment of a glycol with an aqueous solution of 30% sulfuric acid, the same compounds were formed, but with a higher content of tetrahydro-β-ketofuran.

On treatment of 3-methyl-epoxy-2,3-hexyne-4 (II) with an aqueous solution of 20% sulfuric acid, and as a result of repeated distillation of the reaction products, a substance which was a liquid with a specific odor, and which gave a violet coloration with ferric chloride, was obtained. The enol content, determined by the Terentyev-Shcherbakova method, amounted to 85-89%. The elementary composition corresponded to the formula $C_7H_{12}O_2$. On hydrogenation over Raney nickel, hydrogen was absorbed in the quantity required for one double bond. The hydrogenation product was not dehydrated by 30% sulfuric acid. It did not react with hydroxylamine and semicarbazide. With phenyl isocyanate it formed phenylurethan which melted at 86-87° (from ligroin). On the basis of the data obtained, we attributed the structure of tetrahydro-β-ketofuran (VII) to the substance synthesized, and the structure of tetrahydro-β-hydroxyfuran (VIII) to its hydrogenation product:



(VII) (VIII)

EXPERIMENTAL

Isomerization of 3-methyl-epoxy-2,3-hepten-6-yne-4 in acetic anhydride.

20 g of acetic anhydride with 3 drops of H_2SO_4 was placed in a round-bottomed flask with a mechanical stirrer and, with constant stirring, 15 g of the oxide was added gradually. An appreciable evolution of heat resulted. After addition of all the oxide, the reaction mixture was heated on the water bath for 10 minutes, then the reaction product was washed several times with water, and was vacuum steam-distilled. The distilled substance was extracted with ether and dried with Na_2SO_4; the ether was removed, and the substance which remained was vacuum distilled.

A substance with a b. p. of 57-58° at 9 mm was separated after repeated distillation.

n_D^{16} 1.4860; d_4^{16} 0.9091; MR_D 38.5. $C_8H_{10}O$ F F Calc. 36.7.

0.1003 g sub.: 0.2894 g CO_2; 0.0751 g H_2O. 0.1038 g sub.: 0.2980 g CO_2; 0.0793 g H_2O. Found %: C 78.47, 78.35; H 8.40, 8.55. $C_8H_{10}O$. Calculated %: C 78.63; H 8.25.

The semicarbazone was recrystallized twice from aqueous alcohol. Its m. p. was 156° (decomp).

0.0924 g sub.: 19.5 ml N_2 (21.5°, 741.2 mm). 0.0937 g sub.: 19.5 ml N_2 (21°, 749.8 mm). Found %: N 23.51, 23.47. $C_9H_{13}ON_3$. Calculated %: N 23.41.

The oxidation of 3-methyl-hepten-6-yne-4-one-2 was carried out in the cold with potassium permanganate. For the oxidation, 5 g of the ketone was used, and 35.8 g of $KMnO_4$ (34.5 g was required) was used. The manganese dioxide was filtered off, and washed with hot water. No neutral products were observed in the filtrate. The solution was evaporated to a small volume, acidified with 10% H_2SO_4 and boiled under reflux for 2 hours. The cooled solution was alkalized and the neutral products were again driven off in a solution of 2,4-dinitrophenylhydrazine. The precipitate which came down was recrystallized from alcohol, and its m. p. was 110-111°; a test of a mixture with the known, prepared 2,4-dinitrophenylhydrazone of methyl ethyl ketone gave no melting point depression.

None of the volatile acids was detected. The portion of the acidified solution which remained was extracted with ether in an extractor. Oxalic acid, which melted at 182° after 3 sublimations, was separated.

Cyclization of 3-methyl-epoxy-2,3-heptene-6-yne-4

150 ml of water acidified with 2-3 drops of H_2SO_4 was placed in a round-bottomed flask with a mechanical stirrer, and 60 g of the oxide was added gradually. From time to time the mixture was cooled with water, lest the temperature exceed 30-40°, as pointed out earlier [6]; a glycol formed under these conditions. Then 12 ml more of concentrated H_2SO_4 was added to the reaction mixture. Stirring was continued for about 3 hours. The upper layer was separated and steam-distilled until a negative reaction for enol was obtained. The resulting substance was extracted with ether, dried over Na_2SO_4, and the ether was removed. A total of 45 g of a product was separated, which was distilled.

The 1st fraction had a b. p. of 40° (3 mm); the 2nd fraction had a b. p. of 53-54° (1 mm).

The 1st fraction (n_D^{20} 1.4832 d_4^{20} 0.9068,) corresponded to the unsaturated ketone, 3-methyl-hepten-6-yne-4-one-2.

Analysis of the 2nd Fraction

n_D^{20} 1.4985; d_4^{20} 0.9903; MR_D 41.53. $C_8H_{12}O_2F_2$. Calc. 39.18.

0.1063 g sub.: 0.2670 g CO_2; 0.0836 g H_2O. 0.1065 g sub.: 0.2668 g CO_2; 0.0854 g H_2O. 0.1310 g sub.: 11.7 ml CH_4 (16.5°, 760.3 mm). 0.1238 g sub.: 11.3 ml CH_4 (16°, 748.6 mm). 0.1228, 0.1864 g sub.: 14.36 g benzene: Δt 0.31, 0.47°. Found %: C 68.54, 68.37; H 8.80, 8.97; active H 0.376, 0.376. M 141.5, 141.7. $C_8H_{12}O_2$. Calculated %: C 68.51; H 8.63. M 140.2.

The oxime, recrystallized from alcohol, melted at 129-130°.

0.1014 g sub.: 7.9 ml N_2 (20.5°, 762.5 mm). 0.1832 g sub.: 14.1 ml N_2 (18°, 761.2 mm). Found %: N 8.96, 8.94. $C_8H_{13}O_2N$. Calculated %: N 9.02.

Ozonization. In order to demonstrate the position of the double bond, the resulting product was ozonized in chloroform. 5 g of the substance, dissolved in 41 g of chloroform, was used for the ozonization. 2.12 g of ozone was passed for the ozonization, whereas 1.71 g was required for one double bond. The ozonide was decomposed with water. From the ozonolysis products formaldehyde was determined by condensation with dimedon.

For this, the decomposed ozonide was poured into a volumetric flask, and diluted with water to 150 ml. 10 ml was taken from the total quantity; 0.5 g of dimedon was dissolved in 100 ml of water at 90°. 10 ml of the solution of ozonolysis products was added to the dimedon solution, and the solution was heated for 1 hour at 60-70°. The precipitate which came down was filtered off, washed with hot water, and dried at 60-70°. After recrystallization from methyl alcohol the condensation product melted at 188-188.5°. A test of a mixture with the known, prepared compound gave no melting point depression. 0.1067 g of the dimedon condensation product in 10 ml corresponded to 0.1629 g of formaldehyde in 150 ml of ozonolysis products. Formic acid was determined by the Fink method. 0.7168 g of calomel from 20 ml of the ozonolysis product corresponded to 0.5242 g of formic acid, or 0.3418 g of formaldehyde in 150 ml of the ozonide.

In all, 0.5047 g (47.1%) of formaldehyde was determined in the ozonized products.

Hydrogenation of the cyclization product. 13.75 g of the substances was used for the hydrogenation, which was carried out in methyl alcohol over Raney nickel. 4813 ml of hydrogen was consumed, whereas 4783 ml of hydrogen was required theoretically for 2 double bonds. A colorless product with a b. p. of 66-67° at 2 mm was separated:

n_D^{20} 1.4595; d_4^{20} 0.9695; MR_D 40.55. $C_8H_{16}O_2$. Calc. 40.11.

With $FeCl_3$ the hydrogenation product gave no coloration for enol, and it did not react with hydroxylamine and semicarbazide.

0.1398, 0.1493 g sub.: 20.2, 21.2 ml CH_4 (14°, 770.5 mm). Found %: active H 0.619, 0.608. $C_8H_{16}O_2$. Calculated %: active H 0.699.

The original alcohol was recovered by heating the hydrogenation product with 30% sulfuric acid:

B. p. 69-71° at 2 mm; n_D^{20} 1.4565.

0.1536 g sub.: 22.5 ml CH_4 (16°, 765.6 mm). 0.1577 g sub.: 22.9 ml CH_4 (17°, 765.6 mm). Found %: active H 0.618, 0.608. $C_8H_{16}O_2$. Calculated %: active H 0.699.

Cyclization of 3-methyl-epoxy-2,3-hexyne-4

150 ml of 20% sulfuric acid was placed in a round-bottomed flask, and 20 g of the oxide was added gradually. A strong evolution of heat was observed. After addition of the oxide, the reaction mixture was boiled under reflux for 40-45 minutes. After this the reaction product was steam-distilled at constant volume. The resulting substance was extracted with ether and dried; the ether was removed and the product was vacuum distilled. 16 g of a substance was separated:

B. p. 48-49° at 4 mm; n_D^{20} 1.4560; d_4^{20} 0.9592; MR_D 36.40. $C_7H_{12}O_2$F. Calc. 35.33.

0.1016 g sub.: 16.1 ml CH_4 (11°, 749.8 mm). 0.1074 g sub.: 17.9 ml CH_4 (11.5°, 749.8 mm). Found %: active H 0.669, 0.702, which amounted to 85.1, 89.2 of enol, respectively. $C_7H_{12}O_2$. Calculated %: active H 0.784.

Hydrogenation was carried out in methyl alcohol over Raney nickel. 12.67 g of the substance was used, and 2350 ml of hydrogen was passed for hydrogenation; 2358 ml of hydrogen (15°, 753 mm) was required for the hydrogenation. The hydrogenation product was vacuum distilled:

B. p. 86-87° at 13 mm; n_D^{20} 1.4380; d_4^{20} 0.9476; MR_D 36.16. $C_7H_{14}O_2$. Calc. 36.18.

0.1073 g sub.: 19.5 ml CH_4 (11°, 769.9 mm). 0.0704 g sub.: 13.0 ml CH_4 (11.5°, 769.9 mm). Found: active H 0.786, 0.799. $C_7H_{14}O_2$. Calculated %: active H 0.774. 0.1021 g sub.: 0.2422 g CO_2; 0.0980 g H_2O. 0.1051 g sub.: 0.2482 g CO_2; 0.0994 g H_2O. Found %: C 64.73, 64.45; H 10.74, 10.59. $C_7H_{14}O_2$. Calculated %: C 64.57; H 10.84.

Phenylurethan. A mixture of 1 g of phenol isocyanate and 1 g of the substance was left for 12 days in a sealed ampoule. Then the ampoule was heated for 10 minutes on the water bath. After the contents of the ampoule head crystallized, the precipitate was filtered off and recrystallized from ligroin. The m. p. was 86-87°.

0.1553 g sub.: 8.0 ml N_2 (17°, 738.2 mm). Found %: N 5.82. $C_{14}H_{19}O_3N$. Calculated %: N 5.62.

SUMMARY

1. The tri-substituted oxides of the acetylene and vinylacetylene series were transformed to the corresponding tetrahydro-β-ketofurans by reaction with dilute sulfuric acid, the reaction of formation of which proceeded via the glycol.

2. 2-Vinyl-4,5-dimethyl-tetrahydro-3-ketofuran and 2,4,5-trimethyltetrahydro-3-ketofuran, which were not described in the literature, and also their hydrogen products, 2-ethyl-4,5-dimethyl-tetrahydro-3-hydroxyfuran and 2,4,5-trimethyltetrahydro-3-hydroxyfuran, were isolated.

3. The non-enolizing ketone, 3-methyl-hepten-6-yne-4-one-2, was formed by the isomerization of 3-methyl-epoxy-2,3-hepten-6-yne-4 in acetic anhydride in the presence of sulfuric acid.

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Received February 25, 1954

Leningrad State Institute

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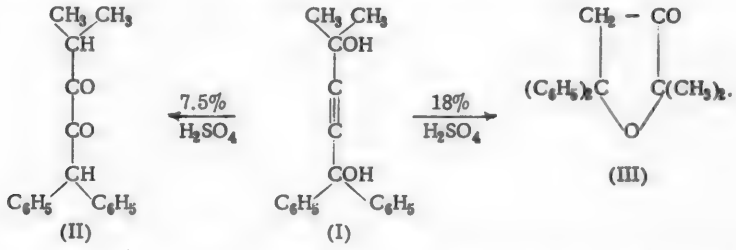
TRANSFORMATION OF ASYMMETRICAL DIMETHYLDIPHENYLBUTYNEDIOL IN AN ACID MEDIUM

IV. 2-METHYL-5,5-DIPHENYLPENTEN-4-OL-2-ONE-3

E. D. Venus-Danilova, V. I. Ryabtseva and L. A. Grigoryeva

The isomerization of asymmetrical dimethyldiphenylbutynediol (2-methyl-5,5-diphenylpentyne-3-diol-2,5) (I) to the saturated α-diketone with an open chain of carbon atoms – 2-methyl-5,5-diphenylpentanedione-3,4 (m. p. 132-133°) (II) – and to a ketone of the tetrahydrofuran series – 2,2-dimethyl-5,5-diphenyltetrahydrofuranone-3 (m. p. 66-67°) (III) – was described earlier [1].

It was observed that a 7.5% alcoholic solution of sulfuric acid converted the glycol only to the diketone, but that an 18% solution converted it to the substituted tetrahydrofuranone. At intermediate sulfuric acid concentrations a mixture of two substances, with a m. p. of 132-133° and a m. p. of 66-67°, was obtained, in which the yield of the cyclic ketone increased, and that of the diketone decreased, with an increase of the acid concentration.

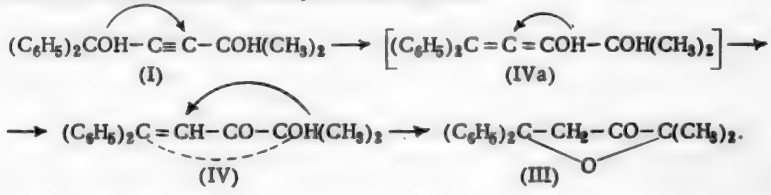


(II) (I) (III)

A further investigation of these transformations, carried out after publication [1], showed that the substance with a m. p. of 132-133° (II) was converted completely to the substance with a m. p. of 66-67° (III) on heating with a 20% alcoholic solution of sulfuric acid.

This fact placed in doubt the problem of the structure of Substance (II), since the diketone should form as a result of a simultaneous bilateral acetylene-allene rearrangement of the glycol, and consequently, is the end product of its isomerization and cannot be converted to tetrahydrofuranone. The tetrahydrofuranones, as shown by Nazarov's works [2], are obtained as a result of the cyclization of unsaturated α-keto alcohols, which are the primary products of the isomerization of the asymmetrical acetylenic γ-glycols, i.e., the products of their acetylene-allene rearrangement. Moreover, in comparison with that required for a unilateral rearrangement which proceeds under milder conditions, an increased sulfuric acid concentration is required for carrying out a bilateral acetylene-allene rearrangement. According to data of the same Report I [1], the diketone (II) developed in 7.5% sulfuric acid, but the tetrahydrofuranone (III) was the product of the cyclization of the unsaturated keto alcohol in the 18% acid.

Proceeding from these considerations, it seemed to us more plausible to assign the structure of the ethylenic α-keto alcohol (IV) to the substance with the m. p. of 132-133°, which formerly was mistaken for the diketone (II). It is possible to assume the following scheme for the isomerization of the acetylenic γ-glycols to the unsaturated γ-keto alcohol (IV) and further to the substituted tetrahydrofuranone (III):



(I) (IVa) (IV) (III)

As a result of a unilateral acetylene-allene rearrangement, the unstable hydroxyallene (IVa) develops first, which, being the enolic form of the unsaturated α-keto alcohol, was converted to the keto alcohol (IV). At a low sulfuric acid concentration (7.5%) this keto alcohol is the sole product of the isomerization of the acetylenic

γ-glycol. With an increase of the acid concentration the cyclization of the keto alcohol [2] proceeds with the formation of tetrahydrofuranone (III).

The simultaneous bilateral acetylene-allene rearrangement of asymmetrically constructed γ-glycols of the acetylene series, with the intermediate formation of dienols, and further, diketones, seemed to us less likely under our conditions. The presence of the considerable dipole moment, and consequently, of the unequal valency of the two hydroxyl groups of these glycols should be considered. Such a bilateral rearrangement is possible for symmetrical γ-glycols of the acetylene series, and leads to diketones, as was observed but incorrectly interpreted by Krestinsky and Bazhenova-Kozlovskaya [3], by the action of formic acid on tetramethylbutynediol.

In Report I [1] the diketone structure was attributed to the substance with a m. p. of 132-133° on the basis of the following data:

1) a negative qualitative reaction with the Grignard reagent for the hydroxyl group;

2) obtaining of the dioxime;

3) obtaining of benzophenone, acetone and oxalic acid by oxidation with potassium permanganate;

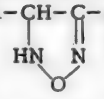
4) obtaining of diphenylacetic acid by oxidation with chromic anhydride;

5) the green-yellow color of the substance.

However, on their critical consideration, none of these arguments are sufficiently conclusive; therefore, we were occupied with a detailed investigation of the substance with a m. p. of 132-133°, and repeated some of the previous experiments and carried out a series of new ones in order to demonstrate the structure of this product.

It was found that on quantitative determination of the number of hydroxyl groups (by Terentyev's method), one hydroxyl group was detected. The negative result of the previous determinations is accounted for, in all probability, by the presence of a carbonyl group in the substance with a m. p. of 132-133°, and also by an insufficient quantity of methylmagnesium iodide and, possibly, by the presence of a stable intramolecular hydrogen bond.

The obtaining of a product of the reaction of the substance with 2,4-dinitrophenylhydrazine, and also of the semicarbazone in the previous experiments, confirmed the presence of one carbonyl group in the substance.

With respect to the dioxime, it was probable that its formation did not take place, but that, instead of it, the isomeric dioxime was substituted 2,3-dihydro-1,2,5-oxdiazole  was formed. This substance could form

as a consequence of the reaction of the unsaturated α-keto alcohol with two molecules of hydroxylamine at the carbonyl and at the double bond, with further cyclization, since the reaction was carried out under very severe conditions.

The original substance was not obtained on heating the reaction product of the substance (m. p. 132-133°) and hydroxylamine with dilute sulfuric acid in order to hydrolyze the dioxime, but strong resinification resulted.

Benzophenone, acetone and oxalic acid could be obtained not only by oxidation of the dienol form of the diketone, but also by oxidation of the ethylenic α-keto alcohol (IV) by potassium permanganate.

With respect to the formation of diphenylacetic acid, obtained by the oxidation of the substance with a m. p. of 132-133° by chromic anhydride, in order to account for its formation it is possible to assume a preliminary hydration of the α-keto alcohol, not according to the Markownikoff rule, as a consequence of its unique structure, and a further oxidation of the dehydration product with the formation of diphenylacetic and hydroxyisobutyric acids; acetone formed from the latter under the conditions of the reaction. Additional experiments were required in order to account for the production of diphenylacetic acid by oxidation of the substance with a m. p. of 132-133°.

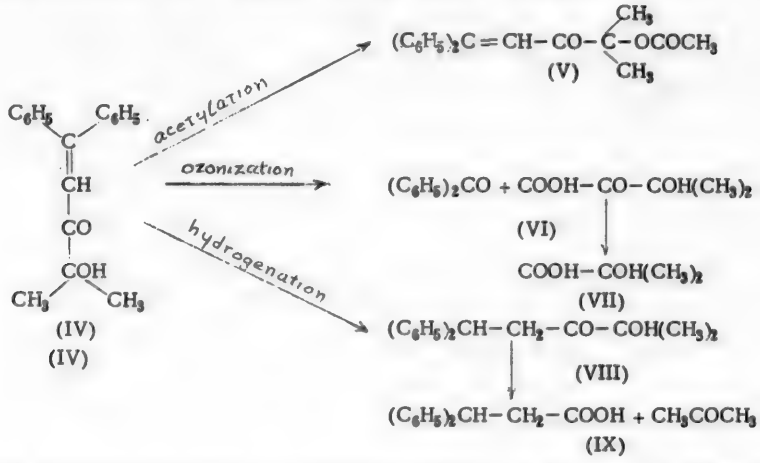
A light-yellow color was characteristic not only of the α-diketones. The ethylenic α-keto alcohols, synthesized for the first time by Scheibler and Fischer [4], and later by Nazarov [2], have the same color. It should be noted that 2-methyl-5-phenylpentene-4-ol-2-one-3, obtained by condensation of dimethylacetylenecarbinol with benzaldehyde, is entirely stable in a neutral and alkaline medium, withstands heating to 200°, and is completely cyclized in an acid medium [2].

In addition to carrying out the previous experiments for the substance with a m. p. of 132-133°, we obtained the acetate of this substance, and carried out an ozonolysis and a catalytic hydrogenation.

The acetate (m. p. 72-73°) (V) was synthesized by the action of acetic anhydride on the substance with a m. p. of 132-133°. The composition of the ester was confirmed by analysis. On hydrolysis of the ester, the original substance with a m. p. of 132-133° was formed.

Benzophenone and α-hydroxyisobutyric acid (VII), which formed as a result of the decomposition of β-methyl-β-hydroxy-α-ketobutyric acid (VI), were obtained by ozonization of the substance with a m. p. of 132-133°.

In the presence of colloidal palladium, the product with a m. p. of 132-133° was hydrogenated to the saturated α-keto alcohol (m. p. 66-67°) (2-methyl-5,5-diphenylpentanol-2-one-3 (VIII), the structure of which was demonstrated by oxidation by lead tetraacetate, to β,β-diphenylpropionic acid (IX) and acetone.



On the basis of all the experiments carried out, it should be considered as demonstrated that the substance with a m. p. of 132-133° is not the diketone (II), but is the ethylenic α-keto alcohol, 2-methyl-5,5-diphenylpenten-4-ol-2-one-3 (IV).

If the saturated α-diketone (II) structure belonged to the original substance (m. p. 132-133°), neither an ester nor α-hydroxyisobutyric acid on ozonization of the substance with a m. p. of 132-133°, nor the β,β-diphenylpropionic acid by oxidation of the reduction product of the substance with a m. p. of 132-133° by lead tetraacetate, could be obtained.

Investigation of the Infrared and Ultraviolet Spectra

For comfirmation of the structure of the substance $C_{18}H_{18}O_2$ (m. p. 132-133°) as the unsaturated α-keto alcohol, 2-methyl-5,5-diphenylpenten-4-ol-2-one-3 (IV), its infrared spectrum* was studied. The spectrum of a specially synthesized [2] α-keto alcohol, $C_{12}H_{14}O_2$ [$(CH_3)_2COH-CO-CH=CH-C_6H_5$], 2-methyl-5-phenylpenten-4-ol-2-one-3 (m. p. 39-40°), was obtained for comparison.

The spectra were taken with an "Infrared Monochromator" ISP-14[b] apparatus with a quartz prism for wavelengths up to 3.5μ and with a rock salt prism for waves from 5μ and above.

The substance $C_{18}H_{18}O_2$. The absorption spectrum was obtained in the region from 1 to 2.5μ and from 5 to 9μ.

The spectrum of the substance in carbon tetrachloride (saturated solution) is given in Fig. 1 (Curve 2); the prism was of quartz, and the cuvette had a depth of 20 mm. As is evident from Fig. 1 (Curve 2), the substance had absorption bands at 1.49, 1.68, 1.76 and 2.07μ. The 1.49μ band is characteristic of the O−H group (first overtone ν); the 2.07 τ band (ν + δ) is also characteristic of this group. The 1.68 μ band corresponds to the benzene ring, and the 1.76 μ band corresponds to the methyl group. For comparison, the spectrum of the solvent, carbon tetrachloride, was presented (Fig. 1, Curve 1).

The presence of the hydroxyl group was also confirmed by the 2.9 μ band (fundamental tone). This band is represented in Fig. 2 (Curve 1). In this case the substance, dissolved in carbon tetrachloride, was photographed by points; the cuvette had a depth of 1.0 mm. It should be noted that the 2.9 μ band was relatively wide. This enabled us to assume the presence in the substance of an intramolecular hydrogen bond, which is not broken on dissolving in

* The spectra were investigated by V. N. Nikitiny, to whom we express our deep appreciation.

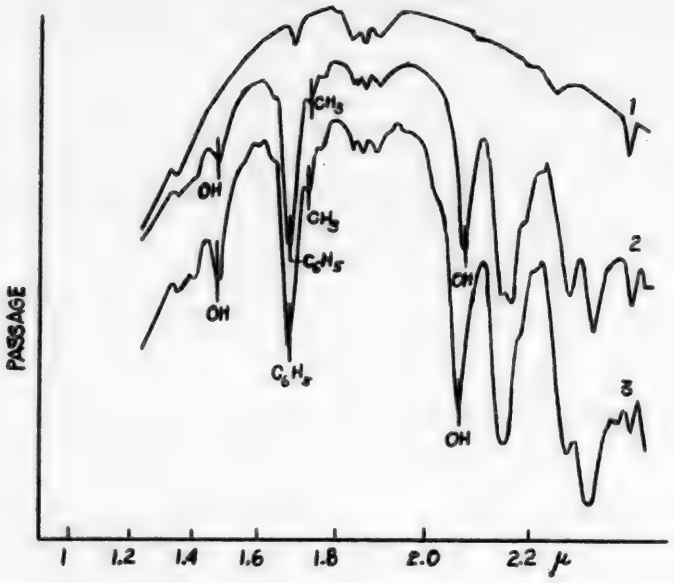


Fig. 1. Infrared spectra; d 20 mm.
1) CCl_4, 2) $C_{18}H_{18}O_2$ in CCl_4, 3) $C_{12}H_{14}O_2$ in CCl_4.

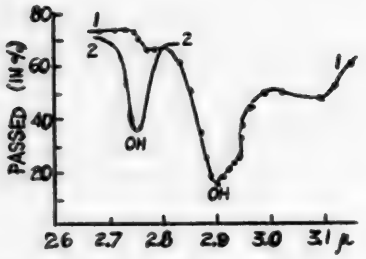


Fig. 2. Infrared spectra; d 1.0 mm.
1) $C_{18}H_{18}O_2$ in CCl_4, 2) C_2H_5OH in CCl_4.

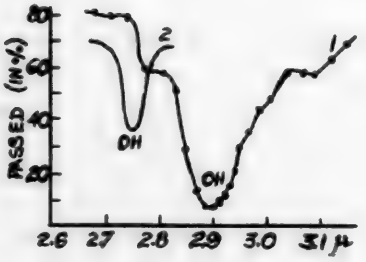


Fig. 4. Infrared spectra; d 1.0 mm.
1) $C_{12}H_{14}O_2$ in CCl_4, 2) C_2H_5OH in CCl_4.

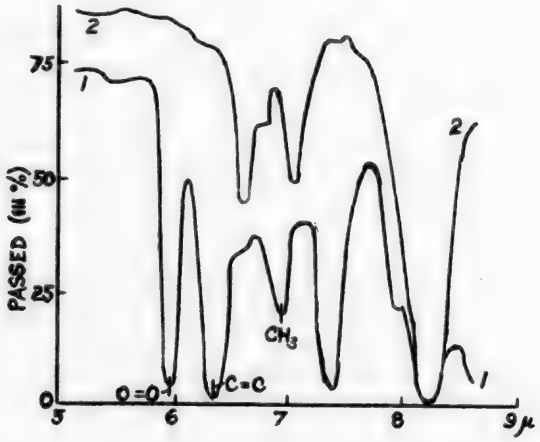


Fig. 3. Infrared spectra; d 0.158 mm.
1) $C_{18}H_{18}O_2$ in $CHCl_3$, 2) $CHCl_3$.

carbon tetrachloride. For comparison, the hydroxyl group band of the ethylenic alcohol, dissolved in carbon tetrachloride, is given in Fig. 2 (Curve 2). This band is considerably narrower, since in this case there are no hydrogen bonds, and it is located at 2.75 μ.

The absorption spectrum of the substance dissolved in chloroform is presented in Fig. 3 (Curve 1). The spectrum was photographed by points with the rock salt prism, and a cuvette depth of 0.158 mm. The 5.98 μ absorption band characterized the vibration of the C=O bond, and the 6.34 and 6.95 μ bands belonged to the C=C and the CH_3 groups, respectively. In order to be sure that the bands observed did not pertain to chloroform, the spectrum of pure chloroform in a layer of 0.158 mm was taken (Fig. 3, Curve 2).

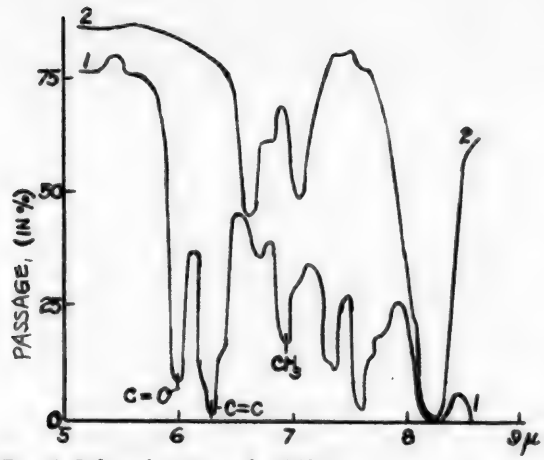


Fig. 5. Infrared spectra; d 0.158 mm.
1) $C_{12}H_{14}O_2$ in $CHCl_3$, 2) $CHCl_3$.

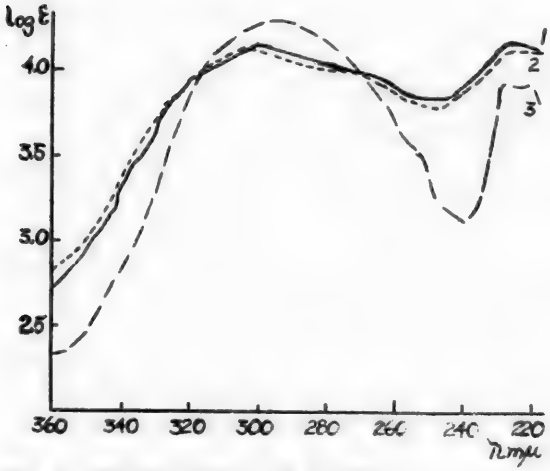


Fig. 6. Ultraviolet spectra in alcohol.
1) 2-Methyl-5,5-diphenylpenten - 4-ol-2; 2) acetate of 2-methyl--5,5-diphenylpenten - 4-ol-2-one-3; 3) 2-methyl-5-phenylpenten--4-ol-2-one-3.

The absorption spectra of the substances $C_{12}H_{12}O_2$ and $C_{12}H_{14}O_2$, which of course have the same functional groups, were close, since they differ by only one phenyl radical.

Thus, the absorption spectra of the substance $C_{12}H_{12}O_2$ indicated the existence of the following groups:

O−H − 1.49, 2.07 μ bands (Fig. 1, Curve 2) and 2.9 μ (Fig. 2, Curve 1),

C=O − 5.98 μ band (Fig. 3, Curve 1),

C=C − 6.34 μ band (Fig. 3, Curve 1), C_6H_5 − 1.68 μ band (Fig. 1, Curve 2),

CH_3 − 1.76 μ band (Fig. 1, Curve 2) and 6.95 μ (Fig. 3, Curve 1).

The substance $C_{12}H_{14}O_2$. This substance was investigated similarly to the preceding. Its spectra are recorded in Figs. 1, 4 and 5. Absorption bands related to the following groups were determined:

O−H − 1.49, 2.07 μ bands (Fig. 1 , Curve 3) and 2.9 μ band (Fig. 4, Curve 1),

C=O − 5.98 μ band (Fig. 5, Curve 1),

C=C − 6.28 μ band (Fig. 5, Curve 1),

C_6H_5 − 1.68 μ band (Fig. 1, Curve 3),

CH_3 − 1.76 μ band (Fig. 1, Curve 3) and 6.92 μ band (Fig. 5, Curve 1).

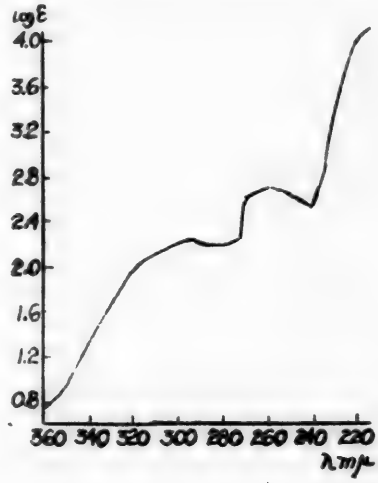


Fig. 7. Ultraviolet spectrum of 2-methyl-5,5--diphenylpentanol-2-one-3 in alcohol.

The ultraviolet spectra were photographed with an SF-4• spectrophotometer.

The absorption curves of alcoholic solutions of 2-methyl-5,5-diphenylpenten - 4-ol-2-one-3 (Substance IV) (Curve 1), its acetate (Substance V) (Curve 2), and 2-methyl-5-phenylpenten - 4-ol-2-one-3 (Curve 3) are presented in Fig. 6. In Fig. 6 the similarity of Curves 1 and 2 and of Curve 3 is seen clearly. In all cases a shift of the absorption maximum toward the long-wave part of the spectrum was observed, which is characteristic of the carbonyl group. The maximum at 302 mμ, ε 13,586 (Curve 1) corresponds to Substance IV, that at 302 mμ , ε 12,792 (Curve 2) to Substance V, and that at 294 mμ , ε 19,604 (Curve 3) to 2-methyl-5-phenylpenten - 4-ol-2-one-3.

In Fig. 7 the absorption curve of the saturated keto alcohol, 2-methyl-5,5-diphenylpentanol-2-one-3 (Substance VIII), is given, which differs sharply from the curves presented in Fig. 6.

• The ultraviolet spectra were taken by T. N. Naugolnaya and Z. A. Dranitskaya, to whom we express our appreciation.

EXPERIMENTAL

The substance with a m. p. of 132-133° was obtained in a yield of 93% as light-greenish, fine, acicular crystals with a m. p. of 132-133° (from alcohol), according to a method described earlier [1], by the action of a 7.5% alcoholic solution of sulfuric acid on a symmetrical dimethyldiphenylbutynediol.

Determination of the Number of Hydroxyl Groups by Terentyev's Method

0.0857 g sub.: 7.4 ml CH_4 (17°, 750 mm). 0.0461 g sub.: 4.0 ml CH_4 (13°, 774 mm). Found %: OH 5.94, 6.26; number of OH-groups: 0.93, 0.98. $C_{18}H_{17}O(OH)$. Calculated %: OH 6.39; number of OH-groups 1.0.

1. The reaction of the substance with a m. p. of 132-133° with 2,4-dinitrophenylhydrazine was carried out exactly according to the procedure of [5], but because of the poor solubility of the substance in alcohol, one and one-half times the quantity of alcohol was used. After 30-40 minutes a bright-red turbidity appeared, and after 24 hours a bright-red precipitate came down, which was filtered off, washed with 60% alcohol and dried in the air. The fine crystals were very soluble in hot alcohol; their m. p. was 202° (decomp.) The substance gave the pyrazoline reaction.

0.0950 g sub.: 0.2236 g CO_2; 0.0454 g H_2O. 0.0951 g sub.: 0.2234 g CO_2; 0.0456 g H_2O. 4.89 mg sub.: 0.524 ml N_2 (22°, 771 mm). 4.28 mg sub.: 0.465 ml N_2 (23.5°, 772 mm). Found %: C 64.19, 64.07; H 5.31, 5.33; N 12.58, 12.70. $C_{24}H_{22}O_3N_4$ (Pyrazoline of the unsaturated keto alcohol). Calculated %: C 64.58; H 4.93; N 12.56. $C_{30}H_{26}O_8N_8$ (Dinitrophenylosozone of the diketone). Calculated %: C 57.51; H 4.15; N 17.88.

According to analytical data, the reaction product of the substance with a m. p. of 132-133° corresponded to the substituted pyrazoline of the unsaturated α-keto alcohol.

2. Action of hydroxylamine on the substance with a m. p. of 132-133°. The experiment described in [1] was repeated, i.e., continued heating of an alcoholic solution of the substance, with hydroxylamine and 2 drops of concentrated hydrochloric acid.* On heating, the solution darkened strongly; after removal of the alcohol a very small quantity of a substance which contained nitrogen (qualitative test) was formed, and after careful purification it melted in the range of 133-142° (decomp.) On heating this substance with a 5% solution of hydrochloric acid for the purpose of hydrolysis, we were unable to separate any individual product, because of resinification.

3. Production of the acetate for the substance with a m. p. of 132-133°. (The acetate of 2-methyl-5,5-diphenylpentene-4-ol-2-one-3). A mixture of 2 g of the substance with a m. p. of 132-133°, 2 g of fused sodium acetate and 8 ml of freshly-distilled acetic anhydride was heated at a slight boil for 5 hours.

After cooling, the solidified substance was diluted with water and partially neutralized with soda. The heavy oil which separated was extracted with ether, the ether extract was washed with a soda solution and with water, and dried with sodium sulfate. After removal of the ether, coarse, colorless crystals were separated, which after several recrystallizations from alcohol had a m. p. of 72-75°.

The resulting product was highly soluble in the usual organic solvents. The reaction for hydroxyl and carbonyl groups was negative. The substance reacted with bromide in chloroform and with potassium permanganate.

11.13 mg sub.: 31.72 mg CO_2; 6.76 mg H_2O. 9.90 mg sub.: 28.32 mg CO_2; 6.15 mg H_2O; 0.1621 g sub.: 16.86 g benzene: Δt 0.16°. 0.2875 g sub.: 0.98 ml 1 N alcoholic solution NaOH. Found %: C 78.78, 78.06; H 6.79, 6.81; M 305.7; saponification equivalent 295.5; % $COCH_3$ 14.54. $C_{20}H_{20}O_3$. Calculated %: C 77.92; H 6.49; M 308; saponification equivalent 308; % $COCH_3$ 13.96.

After hydrolysis of the ester by alcoholic alkali, from the acidified solution a substance with a m. p. of 132-133° separated.

Analytical data showed that the reaction product with a m. p. of 72-73° corresponded to the acetate of the ethylenic α-keto alcohol.

4. Ozonization of the substance with a m. p. of 132-133°. The ozonide, obtained from 2 g of the substance dissolved in 35 ml of chloroform, was decomposed by heating; after addition of several deops of hydrogen peroxide and neutralization of the acids, the neutral products were steam-distilled. 0.28 g of benzophenone with a m. p. of 48° and traces of acetone (reaction with 2,4-dinitrophenylhydrazine and sodium nitroprusside) were found. Benzophenone was also formed in a quantity of 0.82 g from the neutral products, which were non-volatile with steam, and was characterized by a semicarbazone with a m. p. of 164°, which gave no melting point depression with the

* In [1] [J. Gen. Chem., 20, 2227 (1950)] there was a misprint: instead of sulfuric acid it should read hydrochloric acid.

semicarbazone of known benzophenone. The total yield of benzophenone was 80%.

The acidic ozonization products contained α-hydroxyisobutyric acid, which was non-volatile with steam, and a negligible quantity of benzoic and formic acids, which were separated from the hydroxyisobutyric acid by steam-distillation. After evaporation of the ether, the hydroxybutyric acid, in a quantity of 0.42 g (54%) was obtained as a viscous oil which rapidly crystallized. The acid, purified on a porous plate and also by sublimation, had a m. p. of 76.5-78°; no melting point depression was detected in a mixture with known hydroxyisobutyric acid.

0.1929 g sub.: 19.6 ml 0.1 N NaOH. Found: equivalent 98.4. $C_4H_8O_3$. Calculated equivalent 104.

Because of its decomposition with severe blackening, we were unable to analyze the silver salt obtained from the ammonium salt of hydroxybutyric acid and silver nitrate.

The chief ozonization products, benzophenone (80%) and α-hydroxyisobutyric acid (54%), confirmed the assumed structure of the substance with a m. p. of 132-133°, as the ethylenic α-keto alcohol.

Traces of acetone, and formic and benzoic acids were probably formed as a consequence of the partial decomposition of the chief ozonization products.

5. Hydrogenation of the substance with a m. p. of 132-133°. (Production of 2-methyl-5,5-diphenylpentanol--2-one-3). The hydrogenation was carried out in ethyl acetate with a colloidal palladium catalyst. 2.66 g of the substance with a m. p. of 132-133°, 60 ml of ethyl acetate, and at first 5 ml of colloidal palladium (4.5 mg Pd) were used. Catalyst had to be added several times, since the hydrogenation slowed down rather quickly. In all, 12 ml of catalyst was used. The slowly-occurring hydrogenation was carried out until disappearance of the greenish color of the solution; moreover, somewhat more hydrogen was absorbed than was required for one double bond.

After cessation of the hydrogenation the catalyst was filtered off, and the solution of the substance in ethyl acetate was removed from the aqueous layer, and dried with sodium sulfate. The residue quickly recrystallized after removal of the solvent. Purification was carried out by washing the substance on a porous plate with hexane, and recrystallization from a mixture of petroleum and ethyl ethers (1 : 1). Fine, colorless needles, cohering in clusters, were obtained. The m. p. was 66-67°. The yield was 2.2 g (81.8%).

The substance was highly soluble in the usual organic solvents, besides petroleum ether; it reacted energetically with methylmagnesium iodide, and liberated methane; it did not decolorize a solution of bromide in chloroform, but reacted very sluggishly with potassium permanganate.

7.58 mg sub.: 22.33 mg CO_2; 5.13 mg H_2O. 13.52 mg sub.: 39.86 mg CO_2; 9.31 mg H_2O. 0.0317 g sub.: 2.8 ml CH_4 (18°, 757 mm). 0.0501 g sub.: 4.7 ml CH_4 (18°, 757 mm). 0.1400 g sub.: 11.60 g benzene: Δt 0.22°. Found %: C 80.34, 80.41; H 7.57, 7.70; OH 6.25; 6.52; M 274. $C_{18}H_{19}O(OH)$. Calculated %: C 80.60; H 7.46; OH 6.34; M 268.

The 2,4-dinitrophenylhydrazone precipitated rather rapidly on pouring together an alcoholic solution of the substance and an alcoholic solution of 2,4-dinitrophenylhydrazine [5]. After several recrystallizations from boiling ethyl alcohol the m. p. was 208-209°.

0.0909 g sub.: 0.2133 g CO_2; 0.0450 g H_2O. 0.1021 g sub.: 0.2397 g CO_2; 0.0504 g H_2O. 7.42 mg sub.: 0.794 ml N_2 (22°, 766 mm). 7.41 mg sub.: 0.801 ml N_2 (21°, 761 mm), Found %: C 63.99, 64.03; H 5.50, 5.48; N 12.40, 12.54. $C_{24}H_{24}O_5N_4$. Calculated %: C 64.29, 5.36; N 12.50.

According to its properties and to analytical data the substance with a m. p. of 66-67° was the saturated α-keto alcohol.

Oxidation of the substance with a m. p. of 66° by lead tetraacetate. Essentially the oxidation was carried out under the conditions cited in the literature [6], with a few modifications. 1.4 g of the substance with a m. p. of 66-67°, 3 g of lead tetraacetate (29% excess), and 40 ml of 90% CH_3COOH were mixed in a two-necked flask with a mercury seal and a highly efficient reflux condenser. No appreciable evolution of heat was observed. After an hour of stirring, it was heated for 1 hour at 50-60°, also with stirring. It was cooled, diluted with 50 ml of water, and the volatile oxidation products were removed by heating in an alcoholic solution of 2,4-dinitrophenylhydrazine. A yellow precipitate came down at once. Removal was continued until a negative test with a 2,4-dinitrophenylhydrazine solution was obtained. The dinitrophenylhydrazone precipitate was filtered off, washed with water, and recrystallized from alcohol. It consisted of fine, yellow needles with a m. p. of 125-126°; a test of a mixture with the known 2,4-dinitrophenylhydrazone of acetone produced no melting point depression. 0.83 g of the dinitrophenylhydrazone, which corresponded to 0.2 g of acetone (68%), was obtained.

After removal of the acetone the residue in the flask was acidified with dilute hydrochloric acid, the lead chloride was filtered off, washed with ether, and an ether extraction was made from the solution. The residue began to crystallize after drying by sodium sulfate and removal of the ether. A portion of the substance was transferred to a porous plate for removal of the residuals of acetic acid; a portion was dissolved in alkali, and on acidification of the solution with dilute sulfuric acid a solid separated. In both cases an acid with a m. p. of 138-142° was obtained. After recrystallization from a mixture of ether and petroleum ether (b. p. 75-90°) (1 : 2) 0.88 g (74%) of a substance with a m. p. of 148-149° was obtained.

0.1901 g sub.: 8.7 ml 0.1 N NaOH. Found: equivalent 220.9. $C_{15}H_{14}O_2$. Calculated: equivalent 226.

A portion of the acid was converted, via the ammonium salt, to the silver salt, which was analyzed.

0.1178 g sub.: 0.2323 g CO_2; 0.0427 g H_2O; 0.0380 g Ag. 0.0802 g sub.: 0.1581 g CO_2; 0.0289 g H_2O; 0.0258 g Ag. Found %: C 53.78, 53.75; H 4.05, 4.00; Ag 32.26, 32.17. $C_{15}H_{13}O_2Ag$. Calculated %: C 54.05; H 3.90; Ag 32.43.

The analytical data and the properties of the acid corresponded to β,β-diphenylpropionic acid [7], and consequently, the saturated α-keto alcohol was 2-methyl-5,5-diphenylpentanol-2-one-3.

6. Action of 20% sulfuric acid on 2-methyl-5,5-diphenylpentene-4-ol-2-one-3. 2.5 g of the substance with a m. p. of 132-133° and 30 ml of a 20% alcoholic solution of sulfuric acid (H_2SO_4 92%, alcohol 95%) were heated at 65-70° for 5 hours with continuous stirring. On completion of the heating, the color of the solution had almost disappeared. Separation of the reaction product was as usual [1]. A portion of the substance was recrystallized from 95% alcohol, and a portion was recrystallized from petroleum ether; its m. p. was 65-66°. In a mixture with 2,2-dimethyl-5,5-diphenyltetrahydrofuranone-3 no melting point depression was observed, but in a mixture with the original substance there was a sharp depression to 54-58°. The semicarbazone separated very rapidly and melted at 210°. In a mixture with the semicarbazone of tetrahydrofuranone no melting point depression occurred, but with the semicarbazone of the original substance a strong depression occurred.

The tetrahydrofuranone yield was 2.3 g (92%).

SUMMARY

1. It was established that the substance with a m. p. of 132-133°, which formed as a result of the isomerization of asymmetrical dimethyldiphenylbutynediol (2-methyl-5,5-diphenylpentyne-3-diol-2,5), under the influence of a 7.5% alcoholic solution of sulfuric acid, had the structure of the ethylenic α-keto alcohol, 2-methyl-5,5-diphenylpentene-4-ol-2-one-3, and not of the diketone, 2-methyl-5,5-diphenylpentanedione-3,4.

2. An ozonization of this keto alcohol was carried out; the acetate of the keto alcohol, not described in the literature, was obtained.

3. It was shown that the corresponding saturated α-keto alcohol, 2-methyl-5,5-diphenylpentanol-2-one-3, not described in the literature, formed on catalytic reduction of the ethylenic α-keto alcohol.

4. It was observed that, under the influence of a 20% alcoholic solution of sulfuric acid, the ethylenic α-keto alcohol isomerized to 2,2-dimethyl-5,5-diphenyltetrahydrofuranone-3.

5. A mechanism of the isomerization of 2-methyl-5,5-diphenylpentyne-3-diol-2,5 to the ethylenic α-keto alcohol and to tetrahydrofuranone was proposed.

6. The structure of the unsaturated and saturated α-keto alcohols was confirmed by investigation of their infrared and ultraviolet spectra.

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Received February 16, 1954

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TERTIARY TRIATOMIC ALCOHOLS OF THE ACETYLENE SERIES AND THEIR TRANSFORMATIONS

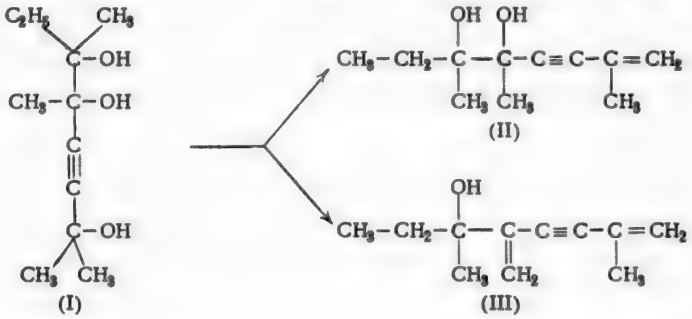
V. DEHYDRATION OF 3,4,7-TRIMETHYLOCTYNE-5-TRIOL-3,4,7

V. I. Nikitin and A. Kh. Khamatov

In a previous report [1] we described the dehydration of 2,3,6-trimethylheptyne-4-triol-2,3,6 by the action on the latter of 20% sulfuric acid, potassium bisulfate or p-toluenesulfo acid. It was shown that the reaction proceeds chiefly with the formation of an α-glycol of the vinylacetylene series, trimethylisopropenylacetylenyl-ethylene glycol. The dehydration of the triol, with the liberation of two molecules of water and the formation of a dienyne carbinol, 2,6-dimethylmethylene-3-pentyne-4-ene-6-ol-2, occurred simultaneously with this to a smaller extent.

In the present report are presented results which we obtained in a study of the action of dehydrating agents on 3,4,7-trimethyloctyne-5-triol-3,4,7 (I), which one of us synthesized for the first time [2] and which is apparently the next homolog of trimethylheptynetriol.

3,4,7-Trimethyloctyne-5-triol-3,4,7 (I) was subjected to the action of 20% sulfuric acid and potassium bisulfate, for which in both cases the chief reaction product was an α-glycol, dimethylethylisopropenylacetylenylethylene glycol (3,4,7-trimethyloctene-7-yne-5-diol-3,4) (II) with a m. p. of 51-52°. The dienyne carbinol, 3,7-dimethyl--4-methyleneoctene-7-yne-5-ol-3 (III), was also always obtained in a small quantity of about 6-8%. A mobile liquid of pleasant odor, and a b. p. of 84-85° (7 mm), it readily polymerized to a dark-red, viscous substance.



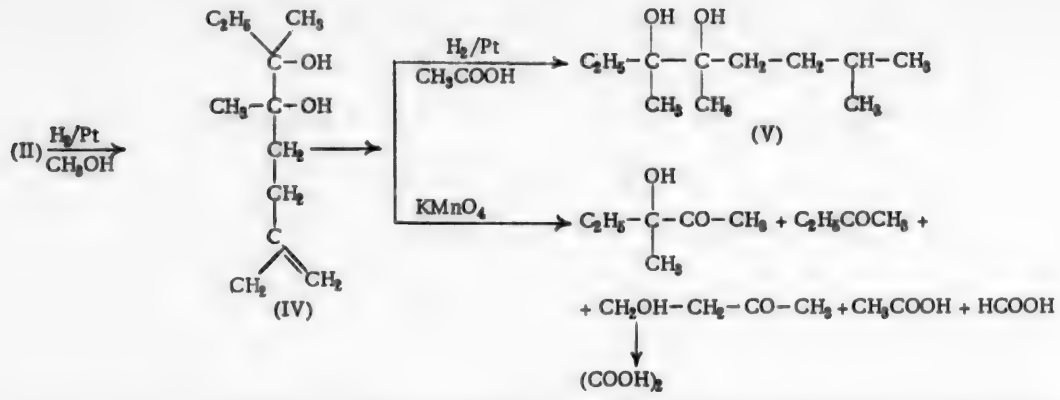
(I) (II) (III)

However, it should be noted that on dehydration of the triol by 20% sulfuric acid, a considerable portion of it resinified, as a consequence of which the yield of the vinylacetylene glycol (II) did not exceed 23%. On vacuum distillation of the same triol over potassium bisulfate at 3-4 mm at a bath temperature of 150-155°, the glycol (II) yield reached 70%.

The structure of the glycol (II) was demonstrated by its oxidation with potassium permanganate; moreover, methyl ethyl ketone, methylethylacetylcarbinol, and formic, acetic and oxalic acids were obtained.

Hydrogenation of the glycol (II) in the presence of a platinum catalyst, in a solution of anhydrous methanol, took place vigorously, but after the addition of two molecules of hydrogen it almost ceased. The ethylenic glycol (IV) obtained at this time boiled at 85-86° (1.5 mm).

Methyl ethyl ketone, methylethylacetylcarbinol, butanol-1-one-3 and formic, acetic and oxalic acids were formed by the oxidation of the ethylenic glycol with potassium permanganate. It can be assumed that the oxalic acid formed as a result of further oxidation of the butanol-1-one-3.

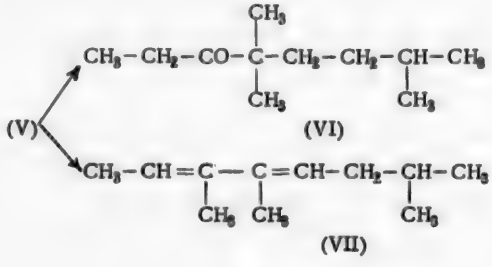


Zalkind and his coworkers [3], and Nazarov and Fischer [4] found that the vinylacetylene series alcohols are readily hydrogenated to the saturated alcohols. At first hydrogenation proceeds at the triple bond until formation of the dienic carbinol, after which further addition of hydrogen is directed to different positions of the conjugated system 1, 2; 3, 4 and 1, 4; $-\overset{1}{C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}H_2$. If hydrogenation ceases after 4 atoms of hydrogen per molecule of the vinylacetylene alcohol are added, then the hydrogenation products are a mixture either of two of the isomeric ethylenic alcohols [3], or of all of the three which are possible [4].

In accordance with this, the formation of three isomeric α-glycols can be expected on hydrogenation of 3,4,7-trimethyloctene-7-yne-diol-3,4 (II). However, on oxidation of the α-glycol which we obtained we separated formic acid, but to all intents and purposes did not observe acetone or isobutyric acid in the oxidation products, which would indicate the addition of hydrogen in the 1,4 or 3,4 position. This condition, and also the formation of other oxidation products corresponding to the glycol, enabled us to assign to the glycol with a b. p. of 85-86° (1.5 mm) the structure of 3,4,7-trimethyloctene-7-diol-3,4 (IV). In glacial acetic acid with the absorption of 1 molecule of hydrogen, the ethylenic glycol (IV) hydrogenates further to the completely saturated glycol, 3,4,7-trimethyloctanediol-3,4 (V).

The structure of the dienynic alcohol (III) was demonstrated by its oxidation with potassium permanganate. Methyl ethyl ketone, and formic, acetic, oxalic and α-hydroxy-α-methylbutyric acids were formed as a result of its oxidation. On hydrogenation of the alcohol (III), 4 molecules of hydrogen were absorbed, which also confirms the structure cited above.

By the action of dilute sulfuric acid (20%) the completely saturated α-glycol, 3,4,7-trimethyloctanediol-3,4,7-trimethyloctanediol-3,4 (V), undergoes transformation in two directions. On the one hand, the pinacoline rearrangement proceeds with the formation of a ketone, apparently 4,4,7-trimethyloctanone-3 (VI); an acid is obtained by its oxidation with bromine in the presence of alkali. On the other hand, trimethyloctanediol (V) was dehydrated, apparently to the dienic 3,4,7-trimethyloctadiene-2,4 (VII), which absorbed 2 molecules of hydrogen on hydrogenation.



EXPERIMENTAL

3,4,7-Trimethyloctyne-5-triol-3,4,7 was prepared by the condensation of dimethylacetylenylcarbinol and methylethylacetylcarbinol by a method described in [2].

B. p. 118-119° (2 mm), d_4^{20} 1.0239, n_D^{20} 1.4796, MR_D 55.45.

I. Dehydration of 3,4,7-Trimethyloctyne-5-triol-3,4,7. Sulfuric acid. A mixture of 13.5 g of 3,4,7-trimethyloctyne-5-triol-3,4,7 and 100 ml of 20% sulfuric acid was heated on a boiling water bath for 30 minutes. The dark-red, oily product which separated was extracted with ether, treated with a dilute soda solution, dried with sodium sulfate, and after removal of the ether was vacuum distilled at 1.5 mm. The following fractions were obtained: 1st fraction, 47-51°, 1.8 g, n_D^{20} 1.4890; 2nd fraction, 72-76°, 3.1 g (23%), crystals with a m. p. of 51-52°; 3rd fraction, 110-114°, n_D^{20} 1.4738 – unreacted 3,4,7-trimethyloctyne-5-triol-3,4,7; a resinified residue, 4.5 g.

Potassium bisulfate. 23.1 g of 3,4,7-trimethyloctyne-5-triol-3,4,7, 7 g of finely pulverized potassium bisulfate and 0.1 g of pyrogallol were placed in a Favorsky flask. The mixture was heated on the bath at 150-155° in vacuo at 3-5 mm. 18.1 g (86%) of a substance distilled at 80-110°. In all, 166.5 g of the triol was dehydrated with potassium bisulfate (in separate portions of 20-25 g), and 139.2 g of dehydration products was obtained.

The crude reaction product was dissolved in ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled: 1st fraction, 78-80° (7 mm), 11.6 g, n_D^{20} 1.4951; 2nd fraction, 80-83° (2 mm), 96.4 g, crystals with a m. p. of 51-52°; 3rd fraction, 110-115° (2 mm), 17.2 g n_D^{20} 1.4750 – unreacted 3,4,7-trimethyloctyne-5-triol-3,4,7.

The crystals dissolved well in the usual solvents, but we were able to recrystallize it from none of the solvents.

Similar fractions from all the experiments were combined and vacuum distilled. Two fractions were separated after several distillations: 1st, 84-85° (7 mm), n_D^{20} 1.5015 – 3,7-dimethyl-4-methyleneoctene-7-yne-5-ol-3 (III); 2nd, 80-82° (2 mm), crystals with a m. p. of 51-52°, apparently 3,4,7-trimethyloctene-7-yne-5-diol-3,4 (II).

Investigation of the Fraction with a B. p. of 84-85° (7 mm).

d_4^{20} 0.9061, n_D^{20} 1.5015, MR_D 53.37. $C_{11}H_{16}O$. Calc. 51.59.

0.1324 g sub.: 0.3894 g CO_2; 0.1196 g H_2O. 0.1028 g sub.: 16.4 ml CH_4 (22°, 688.2 mm). 0.1576 g sub.: 27 ml CH_4 (23.5°, 688.2 mm). Found %: C 80.20; H 10.06; OH 10.17, 10.86. $C_{11}H_{16}O$. Calculated %: C 80.43; H 9.83, OH 10.3.

Oxidation. 16.6 g of the substance in 100 ml of water was used. 500 ml of the 4% solution of potassium permanganate was added dropwise during 3 hours with stirring by a mechanical stirrer, and 76 g more of finely ground potassium permanganate (96 g of $KMnO_4$ from calculation of 9 active oxygen atoms per 1 molecule of the alcohol oxidized) was introduced in small portions during 6 hours. On completion of the oxidation the manganese dioxide was filtered off, and from the filtrate a distillate of neutral substances was removed. After saturation by sodium sulfate 250 ml of the distillate of neutral substances was distilled, and from the latter two fractions were separated by a fractionation column: 1st, 67-71°, 0.6 g, n_D^{20} 1.3878; 2nd, 71-80°, 0.8 g, n_D^{20} 1.3840.

A 2,4-dinitrophenylhydrazone with a m. p. of 113-114° was obtained from both fractions. A test of a mixture with the 2,4-dinitrophenylhydrazone of known methyl ethyl ketone showed no depression.

After removal of the neutral substances the solution was acidified with hydrochloric acid, and the volatile acids were steam-distilled. The distilled volatile acids were neutralized and evaporated to a small volume, acidified with hydrochloric acid and extracted with ether in an extractor. The ether extract was dried with sodium sulfate, and after removal of the ether the acids were distilled: 1st fraction, 90-95°, 2 g; 2nd fraction, 95-110.0°, 5 g; 3rd fraction, 110-115°, 3.1 g.

The 1st fraction was formic acid, which gave calomel with mercuric chloride. The 3rd fraction was acetic acid, which was established by the cacodyl test and by an analysis of the silver salt.

0.0786 g salt: 0.0706 g Ag. 0.0804 g salt: 0.0516 g Ag. Found %: Ag 64.30, 64.17. CH_3COOAg. Calculated %: Ag 64.65.

The solution which remained after removal of the volatile acids was neutralized with alkali, and oxalic acid was precipitated by the action of $CaCl_2$. The calcium salt precipitate was filtered off, dissolved in hydrochloric acid and extracted with ether in an extractor. After removal of the ether 4.1 g of oxalic acid was obtained. Its m. p. was 101-102° (test of a mixture).

After precipitation of the calcium salt the filtrate was acidified with hydrochloric acid and treated with ether. After removal of the ether, 0.5 g of α-hydroxy-α-methylbutyric acid with a m. p. of 71-72° (from a mixture of petroleum ether and benzene) was obtained from the ether extract [5]. A test sample of a mixture with the form of α-hydroxy-α-methylbutyric acid obtained by oxidation of 3,6,7-trimethyloctyne-4-triol-3,6,7 produced no melting point depression.

Thus, methyl ethyl ketone, formic, acetic, oxalic and α-hydroxy-α-methylbutyric acids were obtained as a result of the oxidation of the fraction with a b. p. of 84-85° (7 mm), n_D^{20} 1.5015.

Hydrogenation of 3,7-Dimethyl-4-methyleneoctene-7-yne-5-ol-3. 7.8 g of the substance in a solution of 75 ml of dry methanol was hydrogenated over platinum oxide (according to Adams) for 8 hours. 4600 ml of hydrogen (22°, 690.4 mm) was absorbed. 4760 ml of hydrogen was calculated for 4 moles.

After removal of the methanol the hydrogenation product was vacuum distilled. A fraction with a b. p. of 78-79° (7 mm), apparently 3,4,7-trimethyloctanol-3, was separated.

d_4^{20} 0.8536, n_D^{20} 1.4770, MR_D 53.84. $C_{11}H_{24}O$. Calc. 54.52.

0.1346 g sub.: 0.3784 g CO_2; 0.1703 g H_2O. 0.1622 g sub.: 0.4542 g CO_2; 0.2004 g H_2O. Found %: C 76.68; 76.38; H 13.90, 13.82. $C_{11}H_{24}O$. Calculated %: C 76.65; H 14.05.

Investigation of the Fraction with a B. p. of 80-82° (2 mm), M. p. 51-52°.

0.1666 g sub.: 0.4418 g CO_2; 0.1462 g H_2O. 0.1468 g sub.: 0.3904 g CO_2; 0.1332 g H_2O. 0.1012 g sub.: 29.2 ml CH_4 (17.5°, 696.4 mm). 0.0987 g sub.: 27.9 ml CH_4 (18°, 696.4 mm). Found %: C 72.31, 72.52; H 9.82, 10.15; OH 18.73, 18.48. $C_{11}H_{18}O_2$. Calculated %: C 72.46; H 9.96; OH 18.68.

Oxidation. 18.3 g of the substance in 100 ml of water was placed in a flask equipped with a mechanical stirrer, and 1600 ml of a 4% solution of potassium permanganate (64 g of $KMnO_4$) was added dropwise during 10 hours, with vigorous stirring.

Further investigation of the oxidation products was carried out as in the preceding experiment, as a result of which methyl ethyl ketone and methylethylacetylcarbinol was separated from the neutral products.

Methyl ethyl ketone boiled at 75-80° (1.5 g), its 2,4-dinitrophenylhydrazone melted at 113-114°, and it produced no melting point depression of a test sample of a mixture with the 2,4-dinitrophenylhydrazone of known methyl ethyl ketone. The semicarbazone had a m. p. of 146-147°, which corresponded to the semicarbazone of methyl ethyl ketone (test of a mixture).

Methylethylacetylcarbinol had a b. p. of 147-149° (698.4 mm), n_D^{20} 1.4220. Its 2,4-dinitrophenylhydrazone, with a m. p. of 107-108°, produced no melting point lowering of a test sample of a mixture with the 2,4-dinitrophenylhydrazone of known methylethylacetylcarbinol.

Of the acids the following were obtained: formic, acetic (4.4 g), and oxalic (3.2 g) with a m. p. of 101-102° (test of a mixture).

The presence of the first two acids was established by the calomel and cacodyl tests, and by obtaining the silver salt for acetic acid.

0.1042 g salt: 0.0674 g Ag. 0.0956 g salt: 0.0614 g Ag. Found %: Ag 64.71, 64.22. CH_3COOAg. Calculated %: Ag 64.65.

Thus, methyl ethyl ketone, methylethylacetylcarbinol and formic, acetic and oxalic acids were obtained by oxidation of the crystalline substance with a m. p. of 51-52°.

Hydrogenation of 3,4,7-trimethyloctene-7-yne-5-diol-3,4 in a methanol solution. 13.75 g of the substance in 70 ml of dry methanol was hydrogenated over platinum oxide. 4 liters of hydrogen (21°, 692 mm) was absorbed in 5 hours. Hydrogenation almost ceased after the addition of 4 liters of hydrogen (2 moles). The reaction products were vacuum distilled. 10.5 g of the substance, 3,4,7-trimethyloctene-7-diol-3,4 (IV), was separated.

B. p. 85-86° (1.5 mm), d_4^{20} 0.9337, n_D^{20} 1.4645, MR_D 55.01. $C_{11}H_{22}O_2$. Calc. 55.58.

0.1320 g sub.: 0.3412 g CO_2; 0.1472 g H_2O. 0.0898 g sub.: 0.2328 g CO_2; 0.1000 g H_2O. 0.1569 g sub.: 43.4 ml CH_4 (26.5°, 687.6 mm). 0.1068 g sub.: 29.8 ml CH_4 (26°, 687.6 mm). Found %: C 70.50, 70.69; H 12.47, 12.46; OH 17.06, 17.53. $C_{11}H_{22}O_2$. Calculated %: C 70.90; H 11.91; OH 18.27.

Oxidation of 3,4,7-trimethyloc tene - 7-diol-3,4. 670 ml of a 2% solution of potassium permanganate was slowly introduced during 6 hours into 7.7 g of the substance in 100 ml of water, with stirring by a mechanical stirrer. Investigation of the oxidation products was carried out similarly to the preceding oxidations.

Methyl ethyl ketone (0.8 g) and methylethylacetylcarbinol (1.2 g), which were identified by obtaining their 2, -dinitrophenylhydrazones, were separated from the neutral substances. Moreover, about 0.5 g of a substance

separated, the 2,4-dinitrophenylhydrazone of which melted at 142-143° (from ethyl alcohol).

3.880 ml sub.: 0.730 ml N_2 (22°, 741 mm). 3.970 mg sub.: 0.740 ml N_2 (22°, 741 mm). Found %: N 21.15, 20.96. $C_{10}H_{12}O_5N_4$. Calculated %: N 21.0.

We were unable to carry out any other investigations for this substance, because of its small quantity; but, judging by the analytical data presented above for nitrogen, it can be assumed that it corresponds to butanol-1-one-3.

The solution of the salts, after removal of the neutral substances from it, was acidified with hydrochloric acid, and from it 570 ml of a volatile acid distillate was steam-distilled, for the neutralization of which 237 ml of 0.1 N NaOH was consumed. The presence of formic and acetic acids was established by the calomel and cacodyl tests. 0.5 g of oxalic acid was obtained (test of a mixture) from the non-volatile acids by extraction with ether in an extractor.

Hydrogenation of 3,4,7-trimethyloctene-7-diol-3,4 in acetic acid solution. In the presence of a Pt-catalyst, 6.5 g of the substance [b. p. 85-86° (1.5 mm), n_D^{20} 1.4645] in a solution of 40 ml of glacial acetic acid absorbed 750 ml of hydrogen (800 ml was required for 1 mole of the substance according to calculation). After removal of the methanol the hydrogenation products were distilled, and 4 g of a substance with a b. p. of 107-108° (3 mm), apparently 3,4,7-trimethyloctanediol-3,4 (V), was extracted.

d_4^{20} 0.9220, n_D^{20} 1.4550, MR_D 55.34. $C_{11}H_{24}O_2$. Calc. 56.00.

0.1257 g sub.: 0.3243 g CO_2; 0.1453 g H_2O; 0.1381 g sub.: 0.3574 g CO_2; 0.1577 g H_2O. 0.1347 g sub.: 41.4 ml CH_4 (22.2°, 695.8 mm). 0.1510 g sub.: 44.8 ml CH_4 (27°, 690.1 mm). Found %: C 70.36, 70.68; H 12.53, 12.77; OH 19.79, 18.65. $C_{11}H_{24}O_2$. Calculated %: C 70.23; H 12.85; OH 18.07.

II. Dehydration of 3,4,7-Trimethyloctanediol-3,4 by Sulfuric Acid.

19.2 g of 3,4,7-trimethyloctanediol-3,4 (V) [b. p. 107-108° (3 mm), n_D^{20} 1.4550] was heated with 200 ml of 20% sulfuric acid at 80-90° for 4 hours, with vigorous stirring by a mechanical stirrer.

The reaction products were extracted with ether, neutralized with soda, dried with potash, and after removal of the ether were vacuum distilled. 2 fractions were separated as a result of several distillations at 38 mm: 1st, 97-98°, 5.3 g, apparently the dienic hydrocarbon, 3,4,7-trimethyloctadiene-2,4 (VII); 2nd, 110-112°, 11.62 g, obviously 4,4,7-trimethyloctanone-3 (VI).

Investigation of the Fraction with a B. p. of 97-98° (38 mm)

d_4^{20} 0.8212, n_D^{20} 1.4587, MR_D 50.58. $C_{11}H_{20}$. Calc. 52.06.

0.1300 g sub.: 0.4131 g CO_2; 0.1540 g H_2O. Found %: C 86.68; H 13.25. $C_{11}H_{20}$. Calculated %: C 86.84; H 13.16.

In this fraction the hydroxyl and carbonyl groups were absent.

Hydrogenation. 0.370 g of the substance in a solution of 40 ml of dry methanol was hydrogenated over platinum oxide (according to Adams) for 4 hours. 140 ml of hydrogen was absorbed (27.5°, 688 mm). 135.7 ml of hydrogen for 2 moles was calculated.

Investigation of the Fraction with a B. p. of 110-111° (38 mm)

d_4^{20} 0.8398, n_D^{20} 1.4360, MR_D 52.98. $C_{11}H_{22}O$. Calc. 53.01.

0.1646 g sub.: 0.4647 g CO_2; 0.1898 g H_2O. 0.1288 g sub.: 0.3649 g CO_2; 0.1470 g H_2O. Found %: C 77.49, 77.25; H 12.90, 12.76. $C_{11}H_{22}O$. Calculated %: C 77.56; H 13.03.

A 2,4-dinitrophenylhydrazone with a m. p. of 87-88° was obtained.

6.083 mg sub.: 0.855 ml N_2 (16°, 741 mm). 5.881 mg sub.: 0.840 ml N_2 (22°, 746 mm). Found %: N 15.86, 15.89. $C_{17}H_{26}O_4N_4$. Calculated %: N 16.00.

Oxidation. 5.7 g of substance, 38 g of NaOH and 150 ml of water was introduced into a flask equipped with a mechanical stirrer. 16.1 g of bromine at −10° was slowly introduced dropwise, with vigorous stirring, after which the stirring was continued for 2 more hours. Then the mixture was treated with hyposulfite and the neutral substances were extracted with ether. The ether extract was dried over potash, and after removal of the ether 5 g of crude product was obtained.

4.2 g of a fraction with a b. p. of 110-112° (38 mm), n_D^{20} 1.4324, which was unreacted starting material, was removed by vacuum distillation. After removal of the neutral substances the solution was acidified with hydrochloric acid, and the volatile acids were steam-distilled, neutralized with alkali and evaporated almost to dryness. A silver salt was obtained from the dry residue.

0.0764 g salt: 0.0490 g Ag. Found %: Ag 64.26. CH_3COOAg. Calculated %: Ag 64.65.

The non-volatile acids were extracted with ether in an extractor. After removal of the ether a negligible quantity of a crystalline acid was obtained. The crystals, separated on a porous plate, melted at 93-95°. Because of their small quantity they were not studied closely.

SUMMARY

1. On dehydration of 3,4,7-trimethyloctyne-5-triol-3,4,7, essentially 1 molecule of water split off, by which an α-glycol of the vinylacetylene series formed.

The reaction occurred to a slight extent with the splitting off of 2 molecules of water, as a result of which a certain quantity of the dienynic alcohol formed.

2. On hydrogenation of the vinylacetylene glycol, 3,4,7-trimethyloctene-7-yne-5-diol-3,4, in a methanol solution with a platinum catalyst, only 2 molecules of hydrogen were absorbed and the ethylenic α-glycol, 3,4,7-trimethyloctene-7-diol-3,4, formed.

3. In acetic acid solution in the presence of a platinum catalyst, 3,4,7-trimethyloctene-7-diol-3,4 was hydrogenated to 3,4,7-trimethyloctanediol-3,4.

4. By the action of 20% sulfuric acid, 3,4,7-trimethyloctanediol-3,4 underwent transformation in two directions: on the one hand, the pinacoline rearrangement proceeded with the formation of the ketone, 4,4,7-trimethyloctanone-3 (chief direction of the reaction); on the other hand, the splitting off of two molecules of water proceeded and the dienic hydrocarbon formed.

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Received April 22, 1954

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INVESTIGATION IN THE FIELD OF ALKANE SULFO ACIDS

XII. REACTION OF β-CHLOROETHANESULFOCHLORIDE WITH AROMATIC AMINES

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The study of the reaction of β-chloroethanesulfochloride with aromatic amines was the purpose of the present work.

Earlier we described similar reactions with chloromethane- and α-chloroethanesulfochlorides [1]; they showed that chlorine, in the α-position to the SO_2Cl-group, appeared to have rather great stability and had no tendency toward cleavage. The reaction proceeds by the usual order with the formation of the N-arylamides of chloromethane- and α-chloroethanesulfo acids according to the scheme:

$$RCHClSO_2Cl + 2ArNH_2 \rightarrow RCHClSO_2NHAr + ArNH_2 \cdot HCl, \text{ where } R = H \text{ or } CH_3.$$

The chemistry of β-chloroethanesulfochloride has been little studied. However, from the literature it is known that β-chloroethanesulfochloride behaves unusually with respect to some reagents. Thus, with alcohols it gives the esters, not of β-chloroethanesulfo acid, but of vinyl sulfo acid, according to the scheme [2]:

$$CH_2ClCH_2SO_2Cl + ROH \rightarrow CH_2=CHSO_2OR + 2HCl.$$

It forms the so-called cyclic anhydrotaurine with gaseous ammonia [3]. As with the alcohols, the reaction is accompanied by the splitting off of HCl from the radical. Judging from the literature data, the formation of anhydrotaurine proceeds according to the following equation:

$$CH_2ClCH_2SO_2Cl + 3NH_3 \rightarrow \underset{\underset{NH}{\lfloor\!\rfloor}}{CH_2CH_2SO} + 2NH_4Cl$$

Some authors were inclined to assume that this reaction proceeds without the closing of the ring, with formation of the isomeric anhydrotaurine of the amide of vinyl sulfo acid [4].

$$CH_2ClCH_2SO_2Cl + 3NH_3 \rightarrow CH_2=CHSO_2NH_2 + 2NH_4Cl.$$

The latter assumption is the most likely, since cyclic anhydrotaurine would probably be readily cleaved to taurine, which as a matter of fact was not observed.

The reactions of β-chloroethanesulfochloride with aromatic amines were not described, therefore, it was of interest to study the behavior of chlorine in the β-position to the SO_2Cl-group in reactions of the type mentioned above.

On carrying out the reactions of β-chloroethanesulfochloride with aromatic amines we had in mind first of all to obtain the corresponding derivatives of β-chloroethanesulfo acid, according to the equation:

I. $$CH_2ClCH_2SO_2Cl + 2ArNH_2 \rightarrow CH_2ClCH_2SO_2NHAr + ArNH_2 \cdot HCl.$$

We proceeded from the fact that all these reactions will take place under very mild temperature conditions (water bath or room temperature), and consequently, the cleavage of HCl will not occur. But, considering the literature data, we also did not exclude the possibility of the formation of N-arylsubstituted anhydrotaurine or of the N-arylamides of vinyl sulfo acid:

II. $$CH_2ClCH_2SO_2Cl + 3ArNH_2 \rightarrow \underset{\underset{NAr}{\lfloor\!\rfloor}}{CH_2CH_2SO_2} + 2ArNH_2 \cdot HCl,$$

III. $$CH_2ClCH_2SO_2Cl + 3ArNH_2 \rightarrow CH_2=CHSO_2NHAr + 2ArNH_2 \cdot HCl.$$

The following aromatic amines were used for the reaction: aniline, p-toluidine, p-anisidine, p-phenetidine, and p-nitroaniline; of the heterocyclic amines, α-aminopyridine was used. The reaction with aniline, p-toluidine, p-anisidine and p-phenetidine was carried out in anhydrous ether, that with p-nitroaniline was carried out in pyridine, and that with α-aminopyridine was carried out in dry benzene or acetone.

In all cases compounds were obtained, the chlorine content of which was confirmed by analysis. Consequently, the reaction did not take place according to Scheme I. It could be assumed that it went according to Scheme II, or according to Scheme III. Quantitative analysis gave no possibility of solving this problem, since the reaction products according to both Scheme II and Scheme III had the same qualitative and quantitative compositions. This problem was solved by means of a study of the properties of the compounds obtained. These compounds were similar in properties to the N-arylsulfamides which we described earlier, i.e., they dissolved well in organic solvents and in dilute alkali, were neutral to litmus, and precipitated from alkaline solutions on acidification; they had the capacity to alkylate in alkaline solutions, which was possible only in the presence of a hydrogen or nitrogen atom; finally, with bromine water and potassium permanganate they gave a reaction for a double bond. Not all the properties enumerated were connected with the cyclic structure (Scheme II), but most corresponded to the vinyl sulfo acid derivative (Scheme III).

Thus, we showed that β-chloroethanesulfochloride reacts with aromatic amines just as does 1,2-ethanedisulfochloride, which with aniline forms the anilide of vinyl sulfo acid according to the reaction [5]

$$CH_2SO_2ClCH_2SO_2Cl + 3C_6H_5NH_2 \rightarrow CH_2=CHSO_2NHC_6H_5 + SO_2 + 2C_6H_5NH_2 \cdot HCl.$$

The chlorine in β-chloroethanesulfochloride and the SO_2Cl in 1,2-ethanedisulfochloride are equally unstably bound to the carbon atom, and by the action of aromatic amines are easily split off, together with the mobile α-hydrogen atom, as hydrochloric acid, which at the time of liberation gives a salt with the amines mentioned, and the N-arylamide of vinyl sulfo acid is formed as the chief reaction product.

From these experiments the conclusion follows that the action of aromatic bases on β-chloroethanesulfochloride is similar to the action of an alcoholic alkali solution on the alkyl halides, where the alkali, cutting off the elements of the hydrogen halide, acid from the alkyl halide, leads to formation of ethylene compounds.

As a result of the reactions which we carried out the anilide, p-toluidide, p-anisidide, p-phenetidide, p-nitroanilide and α-aminopyridide of vinyl sulfo acid were obtained and characterized, which considerably extends the data on vinyl sulfo acid derivatives, the chemistry of which has been little studied, although interest in it has increased recently, in connection with its property of forming cation-exchange resins [6].

The resulting compounds were colorless, crystalline, neutral substances (pH 6.9-7.1). They formed in low yields. It is possible that, together with them, the formation of other reaction products which we were unable to separate, also occurs. In any case, the incomplete solution of the crude product was observed on treatment with alkali, and on filtration of the alkaline solution a viscous, gummy, yellow substance remained on the filter.

Some of the compounds obtained were alkylated with methyl iodide in order to demonstrate the presence of a hydrogen atom on the nitrogen. The p-toluidide and p-phenetidide, taken for this purpose, gave well-crystallizing, alkali-insoluble methylation products, N-methyl-p-toluidide and N-methyl-p-phenetidide. Their formation proceeds according to the scheme:

$$CH_2=CHSO_2NHAr + CH_3I + NaOH \rightarrow CH_2=CHSO_2N\begin{matrix}CH_3\\AR\end{matrix} + NaI + H_2O.$$

Together with the amines mentioned above, we carried out the reaction of β-chloroethanesulfochloride with p-aminophenol, but except for a viscous, black substance, we were able to separate nothing. With respect to β-chloroethanesulfochloride, p-aminophenol behaves the same as with the 2-methylethane- and phenylmethanesulfochlorides [7], i. e., the whole reaction mixture resinified in this reaction, in spite of employment of the mildest conditions.

Constants of the resulting compounds are recorded in the Table.

EXPERIMENTAL

I. Production of the Starting Materials

The β-chloroethanesulfochloride required for the work was obtained from dichloroethane according to the following scheme:

Test No.	Formula of compound	Name	Melting point	pH
1	$CH_2=CHSO_2NHC_6H_5$	vinylsulfoanilide	65°	7.38
2	$CH_2=CHSO_2NHC_6H_4CH_3$	vinylsulfo-p-toluidide	73	7.00
3	$CH_2=CHSO_2NHC_6H_4OCH_3$	vinylsulfo-p-anisidide	65	6.95
4	$CH_2=CHSO_2NHC_6H_4OC_2H_5$	vinylsulfo-p-phenetidide	78	7.14
5	$CH_2=CHSO_2NHC_6H_4NO_2$	vinylsulfo-p-nitroanilide	125	–
6	$CH_2=CHSO_2NHC_5H_4N$	vinylsulfo-α-aminopyridide	191	6.5
7	$CH_2=CHSO_2N(CH_3)C_6H_4CH_3$	vinylsulfo-N-methyl-p-toluidide	103 - 105	–
8	$CH_2=CHSO_2N(CH_3)C_6H_4OC_2H_5$	vinylsulfo-N-methyl-p-phenetidide	67 - 68	–

$$CH_2ClCH_2Cl \xrightarrow{NH_4SCN} CH_2ClCH_2SCN \xrightarrow{2HOH + 3Cl_2} CH_2ClCH_2SO_2Cl.$$

We used this method for the first time (other methods of its production are described in the literature [5, 8]).

Preparation of β-chloroethanethiocyanate. 23.03 g (0.3 mole) of ammonium thiocyanate and 60 ml of anhydrous alcohol were added to 30 g (0.3 mole) of dichloroethane. The reaction flask, equipped with a reflux condenser, was heated at a slight boil for 5-6 hours. Then the mixture was cooled, and the ammonium chloride precipitate which came down was filtered off and washed several times on the filter with small portions of anhydrous alcohol. The alcohol was removed from the filtrate. The residue, consisting of β-chloroethanethiocyanate and 1,2-ethanedithiocyanate, which also formed during this reaction, and ammonium chloride, was treated with water. In addition, the ammonium chloride was dissolved, the dithiocyanate remained insoluble as a solid substance, and the β-chloroethanethiocyanate was emulsified with water. The dithiocyanate was separated, washed on the filter with ether, and the β-chloroethanethiocyanate was extracted from the aqueous emulsion with ether. The ether extract was separated from the water and dried with calcium chloride. After removal of the ether on the water bath, the β-chloroethanethiocyanate which remained was vacuum distilled at 91-92° (15 mm). Its b. p. was 202-203° at atmospheric pressure. The yield of β-chloroethanethiocyanate was 4.1 g (11.14%). It was a colorless, oily liquid with a specific pungent odor. The yield of 1,2-ethanedithiocyanate was 5 g (13.6%). It consisted of colorless, hard crystals with a m. p. of 87-88° and a pungent, obtrusive odor, and it possessed lachrymatory and sternutatory action.

0.1539 g sub.: 12.11 ml 0.1 N H_2SO_4. Found %: N 11.02. C_3H_4NSCl. Calculated %: N 11.52. 0.1000 g sub.: 14.15 ml 0.1 N H_2SO_4. Found %: N 19.81. $C_4H_4N_2S_2$. Calculated %: N 19.44.

Production of β-chloroethanesulfochloride. A strong current of chlorine was passed into an emulsion of 27.3 g of β-chloroethanethiocyanate in 100 ml of water for 4 hours. The reaction temperature was kept at from 0 to 7°. A greenish-yellow oil, β-chloroethanesulfochloride, collected at the bottom of the reaction flask. The oil was separated from the water layer, and washed several times with water, with a weak solution of soda (0.5% solution), and again with water. After separation from the water, it was dried with calcium chloride. The resulting sulfochloride was vacuum distilled at 84-86° (15 mm). According to the literature, its boiling point was 125-127° at 30 mm, and 93-96° at 17 mm [8]. The yield was 23 g (62.7%). It was a mobile liquid with a pungent odor and with lachrymatory action.

II. Reactions of β-Chloroethanesulfochloride with Aromatic Amines

Reaction with aniline, p-toluidine, p-anisidine, p-phenetidine and α-aminopyridine were carried out by a method which we described in previous reports [9]; therefore, a detailed description of it is omitted, and only the most essential experimental data are cited below.

Reaction with aniline. 2 g of β-chloroethanesulfochloride and 3.42 g of freshly-distilled aniline in 15 ml of anhydrous ether were used. The anilide of vinyl sulfo acid which separated crystallized with difficulty, only with strong cooling and rubbing with a glass rod. The yield was 0.9 g (40.6%). The reaction carried out at room temperature gave an anilide yield of 31.2%; the reaction carried out without a solvent gave a yield of 14% of the anilide of vinyl sulfo acid.

0.0644 g sub.: 3.44 ml 0.1 N H_2SO_4. 0.0644 g sub.: 0.0826 g $BaSO_4$. Found %: N 7.48; S 17.67. $C_8H_9O_2NS$. Calculated %: N 7.65; S 17.44.

Reaction with p-toluidine. 2 g of β-chloroethanesulfochloride and 3.9 g of p-toluidine in 35 ml of anhydrous ether were used. The yield of vinylsulfo-p-toluidide was 0.91 g (37.3%). It consisted of colorless crystals which were bitter to the taste. The reaction, carried out without heating, gave a yield of 36.1% of the product. As is evident, the temperature did not affect the yield of vinylsulfo-p-toluidine in the present case.

0.0476 g sub.: 2.41 ml 0.1 N H_2SO_4. 0.0696 g sub.: 0.0842 g $BaSO_4$. Found %: N 7.09; S 16.61. $C_9H_{11}O_2NS$. Calculated %: N 7.10; S 16.24.

Reaction with p-anisidine. 1 g of β-chloroethanesulfochloride and 2.3 g of p-anisidine in 25 ml of anhydrous ether were used. The yield of the product was 0.55 g (42.3%); the yield of vinylsulfo-p-anisidide was 23% at room temperature.

0.052 g sub.: 2.41 ml 0.1 N H_2SO_4. 0.1017 g sub.: 0.1135 g $BaSO_4$. Found %: N 6.51; S 15.32. $C_9H_{11}O_3NS$. Calculated %: N 6.57; S 15.02.

Reaction with p-phenetidine. 2 g of β-chloroethanesulfochloride and 5.4 g of p-phenetidine in 40 ml of anhydrous ether were used. The yield of vinylsulfo-p-phenetidide was 0.7 g (25.9%); the yield was 11.1% at room temperature.

0.0526 g sub.: 2.28 ml 0.1 N H_2SO_4. 0.0578 g sub.: 0.0590 g $BaSO_4$. Found %: N 6.09; S 14.01. $C_{10}H_{13}O_3NS$. Calculated %: N 6.17; S 14.09.

Reaction with p-nitroaniline. 2 g of β-chloroethanesulfochloride was added dropwise to a solution of 1.7 g of p-nitroaniline in 10 ml of pyridine. The mixture was heated on a boiling water bath for 2 hours, and then was left for 1 day. The reaction product, vinylsulfo-p-nitroanilide, together with unreacted p-nitroaniline, was precipitated from the pyridine solution by cold, dilute hydrochloric acid. The dark precipitate which came down was filtered off, and was then treated with dilute alkali with slight heating. After separation of the p-nitroaniline, which did not dissolve in alkali, from the alkaline solution, the vinylsulfo-p-nitroanilide was precipitated by dilute sulfuric acid. The yield was 0.6 g (26.5%). It was a finely-crystalline, yellow power, but the yellow color faded considerably during its purification from alcohol and water. The product differed from the other N-arylamides of vinyl sulfo acid in solubility: it was soluble in alcohol, benzene, and chloroform only on heating, whereas the above-described N-arylsulfoamides dissolved in these solvents in the cold.

0.0809 g sub.: 7.00 ml 0.1 N H_2SO_4. 0.1000 g sub.: 0.1036 g $BaSO_4$. Found %: N 12.12; S 14.23. $C_8H_8O_4N_2S$. Calculated %: N 12.28; S 14.03.

Reaction with α-aminopyridine. 1.5 g of β-chloroethanesulfochloride and 1.73 g of α-aminopyridine in 20 ml of anhydrous benzene were used. The yield of vinylsulfo-α-aminopyridide was 0.2 g (11.8%). Conduction of the reaction in acetone gave results similar to those obtained with benzene. The vinylsulfo-α-aminopyridide consisted of fine, colorless crystals, which were bitter to the taste, highly soluble in water in the cold, highly soluble in alcohol on heating, but insoluble in chloroform, ether, benzene, and dichloroethane. Recrystallization was made from alcohol.

0.0355 g sub.: 3.81 ml 0.1 N H_2SO_4. 0.0301 g sub.: 0.0385 g $BaSO_4$. Found %: N 15.03; S 17.56. $C_7H_8O_2N_2S$. Calculated %: N 15.20; S 17.39.

Methylation of vinylsulfo-p-toluidide. 0.45 g of methyl iodide was added to 0.14 g of vinylsulfo-p-toluidide in a solution of 5% alkali. Conduction of the reaction and isolation of the methylated product were carried out analogously to that which we described earlier [9]. The yield of the vinylsulfo-N-(methyl)-p-toluidide was 0.11 g (73.3%). It was recrystallized from alcohol and water. It consisted of fine, colorless crystals, which were sweet to the taste.

0.0481 g sub.: 2.2 ml 0.1 N H_2SO_4. Found %: N 6.40. $C_{10}H_{13}O_2SN$. Calculated %: N 6.63.

Methylation of vinylsulfo-p-phenetidide. 0.16 g of the p-phenetidide of vinyl sulfo acid in 5% alkali and 0.45 g of CH_3I were used. The yield of vinylsulfo-N-methyl-p-phenetidide was 0.14 g (82.3%). It was recrystallized from alcohol and water.

0.0508 g sub.: 2.04 ml 0.1 N H_2SO_4. Found %: N 5.60. $C_{11}H_{15}O_3NS$. Calculated %: N 5.80.

SUMMARY

1. A method of production of β-chloroethanesulfochloride from dichloroethane was proposed.

2. The reactions of β-chloroethanesulfochloride with the following aromatic amines were studied: aniline, p-toluidine, p-anisidine, p-phenetidine, p-nitroaniline, and also with α-aminopyridine.

3. It was found that chlorine in the β-position to the sulfo-group possesses great mobility, as a result of which the above-mentioned reactions proceed with the cleavage of HCl from the radical, and with the formation of the corresponding N-arylamides of vinyl sulfo acid.

4. The anilide, p-toluidide, p-anisidide, p-phenetidide, p-nitroanilide and α-aminopyridide of vinyl sulfo acid were obtained and characterized.

5. The effect of temperature on the yields of the reaction products was shown.

6. The methylation products of the p-toluidide and p-phenetidide of vinyl sulfo acid, by which the structure of the N-arylsulfamides obtained was demonstrated, were obtained and characterized.

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Received February 12, 1954

Voronezh State University

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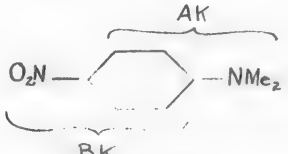
EXTRAMOLECULAR INTERACTIONS AND CHROMATICITY

V. INVESTIGATION OF THE ABSORPTION SPECTRA OF MOLECULAR COMPLEXES OF NITRO COMPOUNDS WITH AROMATIC AMINES•

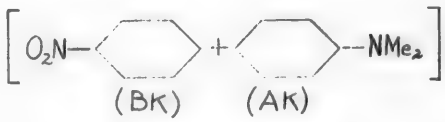
V. A. Izmailsky and A. N. Guseva

The present investigation arose in connection with a study which we carried out for compounds with "separate" non-conjugated chromophoric systems, constructed according to the A – K – Q – K – A or A – K – Q – B – K type, where K is a conjugated system; B is the electrophilic chromophore, for example, NO_2; A is the electron donor chromophore, for example, NMe_2 (Me = CH_3); and Q is the group interrupting the conjugation [1, 4, 5, 6]. We concluded that the color of such compounds arises as a consequence of the interaction of AK (donor-enoid) and BK systems (for example, nitro-enoid) with an external field through exomolecular forces,•• similar to those which lead to formation of colored molecular complexes of the [BK + AK] type. Hence, arose the problem of investigating the absorption spectra of molecular complexes from similarly constructed chromophoric BK and AK components, and of comparing their spectra with those of compounds with separate chromophoric systems mentioned above, and also with conjugated compounds of the B – K – A type in which the same B and A groups are combined through the conjugated system K which had the same π-electron structure as in the corresponding molecular complexes.••• A comparative study of the absorption spectra of the molecular compounds and those of the corresponding compounds with conjugated systems can lead to extremely important results for the theory of chromaticity of organic compounds.

We began our investigations with the simpler compounds, in which K was the benzene nucleus, and expressly, we set ourselves the problem of determining the position of the maximum for the molecular complex from dimethylaniline and nitrobenzene (II), and of comparing it with the position of the maximum in p-nitrodimethylaniline (I):



(I)



(II)

We stopped first at compounds with the A = NMe_2 group, expecting a stronger capacity for complex formation and a larger bathochromic effect as a consequence of the fact that this group possesses stronger electron donor properties than do many other groups, for example, NH_2, OCH_3. On the whole, the mixed chromophoric component AK = $C_6H_5NMe_2$ should possess a greater electrophobicity than the aniline molecule with the NH_2 group.

A study of the spectra of molecular complexes of compounds containing electrophilic nitro groups, with phenols, and particularly with phenolates, was of special theoretical interest.

Molecular complexes of mononitrobenzene (BK) with dimethylaniline (AK) were found to be extremely unstable (see Experimental) in solution; this agrees with the observation that we were also unable to isolate them in the solid state [7, 8, 9]. We measured the absorption spectra in pyridine at a concentration equal to 10^{-3}M for nitrobenzene ($\lambda_{max.}$ 309 mμ, $E_{max.}$ 0.67) for $C_6H_5NMe_2$ ($\lambda_{max.}$ 314 mμ, $E_{max.}$ 1.40), and calculated the absorption curve for the sum [$C_6H_5NO_2$ + $C_6H_5NMe_2$] in pyridine: $\lambda_{max.}$ 314 mμ, $E_{max.}$ 1.90. The spectrum of the joint solution of the complex-forming compounds 1AK : 1BK at a concentration equal to 10^{-3}M (Solution No. 4), and the

• See previous reports [1-3].

•• See p. 110 [1] for the basis of the term [1].

••• See [1] for the symbols and classifications of the chromophoric groups and complex chromophoric systems.

values of $\lambda_{max.}$ and $E_{max.}$ were found to lie extremely close to the calculated sum of the absorption of the components forming the complex (Table 1). Under these conditions, this indicated practically complete dissociation of the complex. The displacement of $\lambda_{max.}$ was entirely negligible: $\Delta\lambda_{max.}$ + 4 mμ ($\lambda_{max.}$ 318 mμ, $E_{max.}$ 2.3). At a concentration equal to 10^{-4}M, $\lambda_{max.}$ was 311 mμ.

TABLE 1

Absorption Coefficients E = log I_0/I of an Equimolar Solution of [$C_6H_5NO_2$ + $C_6H_5NMe_2$] in Pyridine at Concentrations of 10^{-3} and 10^{-4}M

λ, mμ	$C_6H_5NMe_2$	$C_6H_5NO_2$	Calculated for sum [$C_6H_5NMe_2$ + $C_6H_5NO_2$]	Solution No. 4 c = 10^{-3}M	Solution No. 5 c = 10^{-4}M
307	0.80	0.62	1.42	–	–
308	0.92	0.655	1.575	–	–
310	1.13	0.66	1.79	1.52	0.60
311	1.21	0.635	1.845	1.60	0.61
312	1.27	0.61	1.88	1.65	0.61
314	1.37	0.53	1.90	1.70	0.59
315	1.40	0.495	1.895	1.75	0.59
316	1.38	0.46	1.84	2.00	0.58
317	1.38	0.43	1.81	2.20	0.55
318	1.35	0.40	1.75	2.30	0.54
320	1.25	0.35	1.60	1.8	0.49
325	0.695	0.274	0.97	1.38	0.35
330	0.23	0.24	0.46	0.92	0.25
335	0.042	0.215	0.26	0.65	0.21
340	– 0.005	0.197	0.19	–	–
345	–	–	–	0.51	0.20
350	–	0.152	0.15	0.445	0.185
360	–	0.117	0.12	0.33	0.15
370	–	0.072	0.07	0.22	0.11
380	–	0.039	0.04	0.135	0.07

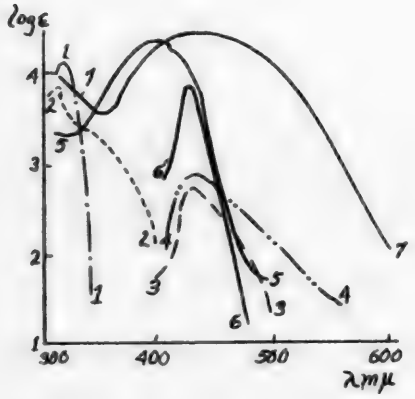


Fig. 1. Formation of molecular complexes from dimethylaniline, p-dimethylanisidine and p-nitrodimethylaniline with nitrobenzene (concentration 10^{-4}M).

1) $C_6H_5NMe_2$ in pyridine; 2) $C_6H_5NO_2$ in pyridine; 3) [$O_2NC_6H_5$ + C_6H_5 + NMe_2] in nitrobenzene; 4) [$O_2NC_6H_5$ + $CH_3OC_6H_4NMe_2$-p] in nitrobenzene; 5) p-$O_2NC_6H_4NMe_2$ in pyridine; 6) [$O_2NC_6H_5$ + + p-$O_2NC_6H_4NMe_2$] in nitrobenzene; 7) p-$O_2NC_6H_4CH$= =$CHC_6H_4NMe_2$-p' in pyridine.

Only a small increase of absorption was found in the 400-430 mμ region at a concentration of $2 \cdot 10^{-2}$, with 3-fold excess of one of the components (experiments with Solutions No. 6 and 7 in pyridine), and with the use of the differential method of spectroscopy (see further). Thus, the nitrobenzene and dimethylaniline complex was extremely unstable and was almost completely dissociated even under conditions otherwise favorable for the formation of a complex.

We were able to determine the position of $\lambda_{max.}$, only by using nitrobenzene in an extremely large excess, namely, as a solvent. In this case it can be assumed that the equilibrium AK + BK $\rightleftharpoons$ [AK⌒BK] is strongly shifted toward formation of the complex. For [$C_6H_5NO_2$ + + $C_6H_5NMe_2$] $\lambda_{max.}$ was 429 mμ (Fig. 1, Curves 1, 2, and 3). The low values of E indicated that even in nitrobenzene the complex is highly dissociated at concentrations of 10^{-3} and 10^{-4}M (solutions No. 8 and 9, Table 2).

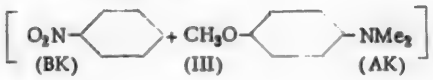
We have postulated [1, 15] that the interaction through exomolecular forces between molecules in the complexes may bring about the formation of a special type of partial electronic bond with the participation of π-electrons. Such a bond differs from the ordinary π-bond by the

absence of an associated σ-bond; therefore, we consider it expedient to propose for it the special name of exo-bond and a special designation by the conjugation symbol (⌒) (better not dotted) with the symbol of the partial bond (AK⌒BK).

The formation of an exo-bond as a result of the linear association of two molecules is theoretically possible. In this instance the exo-bond would probably arise between the π-electrons, along a line perpendicular to the axis of the π-electrons (exo-π-bond). However, there are reasons for assuming that the bond in the complexes considered and in other types (intermediate reaction complexes) is usually brought about through an exo-ρ-bond as a result of a stratified association between the flat molecules lying in parallel planes. This bond arises between the π-electrons of two parallelly (or almost parallelly) situated molecules, and acts along a line connecting the axes of their π-electron clouds.

The capacity of the nitro compound (BK) for interaction and complex formation is probably increased by an increase of the electrophilicity of the compound through the introduction of additional nitro groups. Therefore, a study of the spectra of complexes with dinitrobenzene and with 2,4-dinitrostilbene is of great interest. Considering our previous observations on the greater force of the chromophoric action of the contra-polarized systems with para-positions of two electrophilic or electrophobic groups [4, 10, 11], it can be expected that the spectra of molecular complexes of the aromatic amines with p-dinitrobenzene will be shifted bathochromically, compared with the m-dinitrobenzene complexes in which there is a syn-polarizing system.

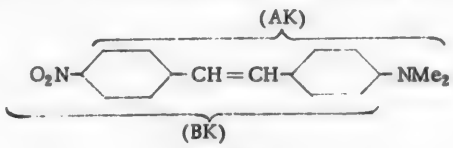
On the other hand, the capacity for interaction and complex formation of the donor-enoid AK system probably is increased through an increase of the total electrophobicity of the compound. We undertook a study of the effect on the $\lambda_{max.}$ position of an increase of the total electrophobicity of the AK system through introduction of a second donor group, for example OCH_3 (III) or $NHCOCH_3$ (Solutions of N,N-dimethyl-p-anisidine No. 11 and 12). In the present case, the introduction of OCH_3 had only a negligible effect on $\lambda_{max.}$ (+ 2 mμ), but judging from the E value (Table 2, Solutions No. 8 and 11, 9 and 12) the complex was actually somewhat more stable. But it was of greatest interest that the absorption region for the complexes (II) and (III) was displaced on the absorption region of the compound with a conjugated system (I) (Fig. 1, Curves 4 and 7).



(in nitrobenzene for c = 10^{-3}M $\lambda_{max.}$ was 431 mμ).

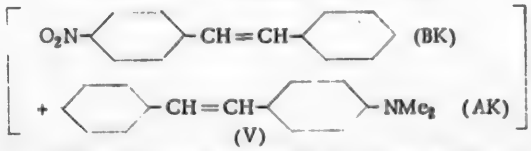
In nitrobenzene an unexpected increase of the molar absorption coefficient values was observed (Table 2, Solutions No. 8 and 9, 11 and 12) for more dilute solutions of complexes (II) and (III) at a concentration of 10^{-4}M, compared with a solution of 10^{-3}M. We assumed that these deviations were possibly a consequence of the spectrum measurement conditions, and were perhaps connected with the wide aperture. This condition showed no effect on the position of the maximum.

Further, it could be expected that the more stable molecular complexes and the phenomenon of the deeper color were perhaps obtained by an increase of the lengths of the conjugated π-electron systems. Therefore, we assumed that the capacity for complex formation would probably be more strongly expressed for the 4-nitrostilbene and the 4-dimethylaminostilbene and, proceeding from the above-indicated considerations, we understood a comparative study of the spectra of 4-nitro- dimethylaminostilbene (IV) and the corresponding molecular complex (V):



(IV)

(in pyridine $\lambda_{max.}$ was 450.5 mμ,
in nitrobenzene $\lambda_{max.}$ was 450 mμ).



(V)

(In pyridine with excess BK $\lambda_{max.}$ was 438 mμ;
with excess AK $\lambda_{max.}$ was 438 mμ.

For the [nitrostilbene + dimethylaminostilbene] complex, regardless of the presence of longer conjugated systems, the stability of the complex with a 1AK : 1BK ratio was insufficient to the same extent as a concentration of 10^{-4}M (Solution No. 18), and even at a concentration of 10^{-3}M (Solution No. 19) the spectral absorption curve was only negligibly shifted toward the longer waves, compared with the spectrum calculated for the sum of the absorption of both original compounds forming the complex. The absorption maximum of 350 mμ almost coincided with that calculated for the sum of the initial compounds (λ_{max} 355 mμ) (Fig. 2, Curves 3,4) at a concentration of 10^{-4} M, and at a concentration of 10^{-3}M the bathochromic displacement amounted to only + 30 mμ ($\lambda_{max.}$ 385 mμ). At a 1 AK : 1BK equimolar ratio of components, even at a concentration of the complex of 0.02 M, we were unable to observe the maximum expected in the region of about 430 mμ. As a consequence of the insufficient solubility of the dimethylaminostilbene in pyridine, a further increase of the concentration was impossible.

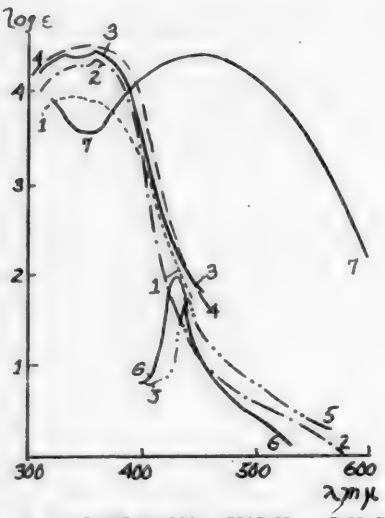


Fig. 2. [4-$O_2NC_6H_4CH{=}CHC_6H_5$ + $C_6H_5CH{=}CHC_6H_4NMe_2$-4] in pyridine. (BK) (AK)

1) BK, concentration 10^{-4}M; 2) AK, concentration 10^{-4}M; 3) sum of absorption curves 1 and 2) 4) [AK + BK], concentration 10^{-4}M; 5) [AK + BK], concentration 0.02 M at a 1AK : 3BK ratio of components (reference solution: 0.04M BK); 6) [AK + BK], concentration 0.02 M at a 3AK : 1BK ratio of components (references solution: 0.04M AK); 7) p-$O_2NC_6H_4CH{=}CHC_6H_4NMe_2$-p', concentration 10^{-4}M.

Thus, we decided to seek a method by means of which it would be possible to determine the maximum of the complex under those conditions when we could not use as the solvent one of the compounds which formed the complex. Such a method was found in the use not only of a higher concentration, but also of an excess of one of the compound, which reacted among themselves with formation of a complex (n moles per 1 mole of the complex), and in the use of the differential method for spectroscopy:* a solution containing (n – 1) M of the compound taken in excess, and appearing at the same time as the solvent for the complex, was used as the reference spectrum. Thus, for example, when the ratio of complex-forming compounds in the solution amounted to 1AK : 3BK (i. e., for 1 mole of the AK compound 3 moles of the BK compound was used, n = 3), a solution containing 2 moles of compound BK (3 – 1 = 2) was used as the solvent and as the reference solution.

Thus, using the indicated differential method of spectroscopy, a 3-fold excess of one of the components and a concentration of 0.02 M (experiments with Solvents No. 20 and 21), we were able to determine $\lambda_{max.}$ for complex (V) (Fig. 3).

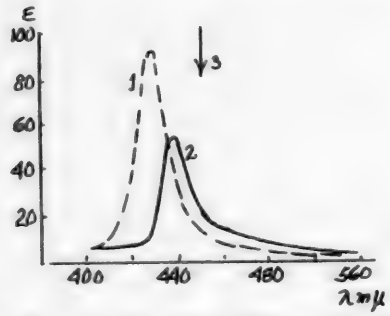


Fig. 3. [p-$O_2NC_6H_4CH{=}CHC_6H_5$ + $C_6H_5CH{=}CHC_6H_4NMe_2$-p'], concentration of [AK + BK] (BK) (AK) in pyridine 0.02 M.

Molar ratio of components: 1) 1AK : 3BK (reference solution: 0.04 M BK in pyridine); 2) 3AK : 1BK (reference solution: 0.04 M AK in pyridine); 3) p-$O_2NC_6H_4CH{=}CHC_6H_4NMe_2$-p' in pyridine, concentration 10^{-4}M, $\lambda_{max.}$ 450.5 mμ.

In complex (V) the absorption maximum, in relation to the maximum calculated for the sum of the components (calculated: $\lambda_{max.}$ 355 mμ, $\epsilon_{max.}$ 31,680, see Solution No. 17), was bathochromically displaced extremely strongly with respect to the calculated maximum and, namely, for 1AK : 3BK a $\lambda_{max.}$ of 438 mμ (+83), was found and for 3AK : 1BK a $\lambda_{max.}$ of 430 mμ ($\Delta\lambda$ + 75) was found. The low values of $E_{max.}$ and $\epsilon_{max.}$ (Solutions No. 20, 21) indicated the strong dissociation of the complex. Therefore, the ε values had only conditional ("formal") value (Fig. 2, Curves 5, 6 and 7).

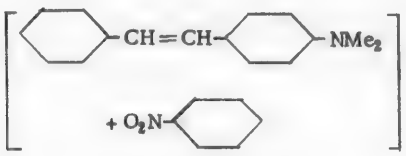
If we found that under these conditions a determination of the maximum for complex [$C_6H_5NO_2$ + $C_6H_5NMe_2$] was impossible as a result of the strong dissociation, then we

* As the experiments of A. V. Belotsvetov showed, this method does not apply when one of the compounds forming the complex has a strong absorption in the visible region of the spectrum, for example for dimethylaminoazobenzene.

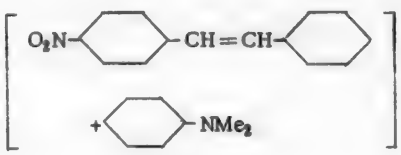
could conclude that an elongation the the conjugated π-electron systems in the components actually increases their capacity for formation of a complex. Moreover, the observed bathochromic displacement of $\lambda_{max.}$ was similar to that which we observed in the interaction of similarly constructed chromophores in conjugated systems as a result of the elongation of the K-system (cf. [3]).

Thus, we found that through exomolecular interaction of the compounds forming the complex we might obtain an effect of complex (V) from the stilbene components, very close to the effect in a conjugated system (IV).

The conjugated systems were increased in both the AK and BK components in complex (V). In order to obtain comparable data on the influence of the lengths of the conjugated chain, we undertook a study of the same spectra of the molecular complexes, with an increase of the lengths of the conjugated system only in one of the components AK or BK, and the scope of the investigation included the system [dimethylaminostilbene + nitrobenzene] (VI), and, on the other hand, [nitrostilbene + dimethylaniline] (VII).



(VI)



(VII)

(in nitrobenzene $\lambda_{max.}$ was 428 mμ, in dimethylaniline $\lambda_{max.}$ was 358 mμ).

For complex (VI) a $\lambda_{max.}$ of 428 mμ, i. e., an actual reduction of the bathochromic effect, compared with the complex (V), was found. However, here also the absorption region was shifted toward the spectrum region of compound (IV) (Fig. 4, Curves 1 and 2).

In a study of the absorption spectra of molecular complexes with p-dimethylaminostilbene, we encountered its insufficient solubility in alcohol. Because of this we decided to use pyridine as the solvent.

It is necessary to note here that generally the solvent had an extremely great effect on the stability of the complexes and on their color. During the investigation of the molecular complexes of quinoline and pyridine salts with the aromatic amines [2,3], we encountered an influence of the solvent on the spectrum and on the stability of the complex.

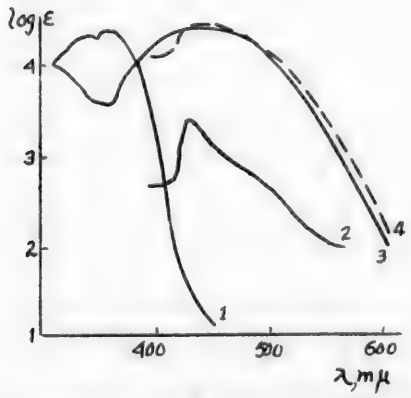


Fig. 4. Solutions of 4-dimethylaminostilbene and 4,4'-nitrodimethylaminostilbene in pyridine and nitrobenzene.
1) 4-Dimethylaminostilbene in pyridine, concentration 10^{-4}M; 2) the same in nitrobenzene, concentration 10^{-4}M; 3) 4,4'-nitrodimethylaminostilbene in pyridine, concentration 10^{-5}M; 4) the same in nitrobenzene, concentration 10^{-5}M.

The molecular complexes were more stable in pyridine than in ethanol. In benzene and in ether a complete disappearance of the optical effect of the interaction of the compounds which formed the complex was often observed in benzene and in ether.

In complex (V), with an excess of dimethylaminostilbene (AK), we observed a hypsochronic effect ($\lambda_{max.}$ 430 mμ), compared with the solution containing an excess of nitro component (BK) ($\lambda_{max.}$ 438 mμ). Apparently, here we have a manifestation of a frequently observed rule. Thus, for systems containing a large excess of dimethylaniline in relation to the nitro compounds, the effect of the interaction in a number of cases disappeared; no formation of a complex with an absorption in the region of about 430 mμ was observed with the use of dimethylaniline as the solvent. Whereas for p-dimethylaminostilbene in nitrobenzene (VI), $\lambda_{max.}$ was 428 mμ, for a solution of p-nitrostilbene in dimethylaniline (VII) we observed only a $\lambda_{max.}$ 358 mμ, i. e., the effect was almost absent.

It was of further interest to explain whether the interaction of nitrobenzene, with a bathochromic effect, on a molecule in which the dimethylamino group was conjugated

with a nitro group system, was possible. In the p-nitrodimethylaniline molecule we actually observed this capacity: a strong bathochromic displacement of the maximum $\lambda_{max.}$ 429 mμ, instead of 390-395 mμ, indicated the formation of the complex [$p\text{-}O_2NC_6H_4NMe_2 + C_6H_5NO_2$] (Fig. 1, Curves 5 and 6).

The capacity of p-nitrodimethylaniline for intermolecular interaction with the nitrobenzene which we established agrees with Gibson and Loeffler's observation for p-nitroaniline [16]. However, these authors did not study the absorption spectra, and their conclusion was made on the basis of an investigation of the transmission of light by an equimolar mixture of p-nitroaniline and nitrobenzene. The conclusion of the intermolecular effects was made on the basis of the observation that a bend of the curve at about 465 mμ changed its position under the influence of pressure. Moreover, the authors noted that in the longer wave regions (500-600 mμ) absorption was found to be insensitive to pressure and therefore, should probably be attributed to the p-nitroaniline itself. However, it should be considered that the absorption of p-nitroaniline itself disappears in the longer wave regions, about 470 mμ [17].

Unlike p-nitromethylaniline, the p-nitrodimethylaminostilbene molecule was found to be extremely stable with respect to nitrobenzene. The change of the spectrum in nitrobenzene was shown to be very small; there were two indistinctly expressed peaks at 452 and 448 mμ.• On the average, according to the half-width of the band, the maximum lies at 450 mμ. This value agrees with the maximum of 450.5 mμ for p-nitrodimethylaminostilbene in pyridine (Fig. 4, Curve 3 and 4).

From these observations it can be concluded that in the 4-nitro-4'-dimethylaminostilbene molecule the system is so much closed in itself (as a result of mutual intramolecular effects) that it has little capacity for extramolecular interactions. If this conclusion is correct, then a sharp difference in the effects of polar and non-polar solvents on the absorption spectra (on the position of the maximum and the molar absorption coefficient) should be absent.

EXPERIMENTAL

A. Synthesis and Purity Ratings of the Preparations

Nitrobenzene was purified by freezing and by distillation. Its b. p. was 209°.

Dimethylaniline – the commercial preparation – was freed from the monomethyl derivative by treatment with acetic anhydride, by steam-distillation of the dimethylaniline, and then by sublimation. Its b. p. was 193°.

p-Dimethylanisidine was obtained by methylation of p-anisidine with dimethyl sulfate. It was purified by steam-distillation and by recrystallization from 50% alcohol. It consisted of white leaflets. Its m. p. was 48°.

p-Nitrodimethylaniline was obtained by methylation of p-nitroaniline with a methyl ester of p-toluenesulfo acid. It was freed from the monomethyl derivative by treatment with acetic anhydride and by steam-distillation. Its m. p. was 162°.

4-Nitro-4'-dimethylaminostilbene was obtained in our laboratory by P. I. Samokish by the condensation of 4-nitrophenylacetic acid (m. p. 150.5-152°) with 4-dimethylaminobenzaldehyde in the presence of piperidine. After recrystallization from alcohol and then from pyridine it consisted of bright-red crystals with a m. p. of 149.5-150° [12].

4-Nitrostilbene was obtained by P. I. Samokish by the condensation of 4-nitrophenylacetic acid with benzaldehyde in the presence of piperidine. From ethyl alcohol the needles were of a light-yellow color with a m. p. of 154-155° [13].

For the first time, 4-dimethylaminostilbene was obtained from anhydrous alcohol, as colorless leaflets with a m. p. of 147-148° by the distillation of 4-dimethylaminophenylbenzylcarbinol under reduced pressure [14].

We selected a new method, namely, the condensation of phenylacetic acid and p-dimethylaminobenzaldehyde in the presence of piperidine. 10 g of p-dimethylaminobenzaldehyde, carefully mixed with 10 g of pure phenylacetic acid and 5 ml of piperidine, was heated for 4 hours at an internal temperature of 140-150° in a three-necked flask equipped with a thermometer and a mechanical stirrer. On completion of the heating, the mixture was treated with boiling water (several portions). The residue was recrystallized from pyridine.

From pyridine and from anhydrous alcohol it consisted of light-weight, colorless leaflets with a m. p. of 147.5-148°, which agreed with the literature values [14].

• On a logarithmic curve these peaks disappeared.

On long storage the crystal surfaces became brownish, therefore, we had to use only the freshly-recrystallized preparation for the spectroscopic measurements.

B. Investigation of the Absorption Spectra

The spectroscopic measurements were carried out with a Beckmann photoelectric photometer at a layer depth of 1 cm for the most part, which offered no possibility of carrying out spectrum measurements at higher concentrations. Later we used quartz inserts (Schultz plates) in a cuvette of 1.0 cm in order to obtain layers with a depth of 0.10 and 0.01 cm.

The measurements were carried out through every 5 mμ, but through every 1-2 mμ in the positions of maxima and bends.

The molar absorption coefficient ε was probably not accurately determined, as a consequence of the fact that the complex was dissociated to a greater or lesser extent and its concentration was unknown. The calculated values of ε can be used only conditionally for comparison of the degrees of complex formation. Essentially, we had to consider the absorption coefficients $E = \log I_0/I$, in investigation of the spectra of the complexes.

The essence of the differential method which we used for the investigation of the spectra of the complex compounds is stated above (p. 1407).

1. Investigation of Solutions of [Nitrobenzene + Dimethylaniline] (Complex II)

Symbols: AK = $C_6H_5NMe_2$; BK = $C_6H_5NO_2$.

a) Solutions in ethanol.

No. 1. The solution of equimolar quantities of the components (1AK : 1BK), at a concentration equal to 0.02 M for each compound, was not colored. No maximum was observed in the 400-430 mμ region. There was dissociation of the complex.

No. 2. At a concentration of 0.1 M for each component, 1AK : 1BK, a yellow color appeared; however, the formation of a complex became insignificant in this case also, so that a maximum was absent in the 400-430 mμ region. For example, the following E values in the presence of some interaction were found:

λ mμ	400	410	420	430	440
E for solution No. 1	0.414	0.179	0.067	0.024	0.013
E for solution No. 2	1.32	0.705	0.420	0.302	0.234

No. 3. The solution had an AK concentration equal to 0.2 M and a BK concentration equal to 0.02 M. (10AK : 1BK). Because of strong absorption, the spectrum could not be measured with a cuvette of 1 cm.

b) Solutions in pyridine. They were considerably more deeply colored than in alcohol at the same concentrations.

No. 4. With an equimolar ratio (1AK : 1BK) and concentration for each component equal to 10^{-3} M, a $\lambda_{max.}$ of 318 mμ and an $E_{max.}$ of 2.3 was found (Table 1).

No. 5. For each of the components a $\lambda_{max.}$ of 311 mμ, and a $E_{max.}$ of 0.61 (Table 1) was found at an equimolar ratio of 1AK : 1BK and a concentration equal to 10^{-4} M.

No. 6. At a 3AK : 1BK ratio and an AK concentration equal to 0.6 M, and a BK concentration of 0.02 M (reference solution: 0.04 M AK in pyridine), no maximum was observed in the region of about 330 mμ.

No. 7. With a 1AK : 3BK ratio and an AK concentration of 0.02 M, and a BK concentration of 0.06 M (reference solution: 0.04 M BK in pyridine), no maximum was observed in the region of about 330 mμ.

c) Solutions in nitrobenzene. The ratio was 1AK : ∞ BK.

No. 8. For a solution of $C_6H_5NMe_2$ in nitrobenzene, at a concentration of $1 \cdot 10^{-3}$ M $\lambda_{max.}$ was 429 mμ, and $E_{max.}$ was 0.20 (Table 1).

The color of the solution was yellow-orange.

No. 9. For a solution of $C_6H_5NMe_2$ at a concentration equal to $0.95 \cdot 10^{-4}$ M, $\lambda_{max.}$ was 428.5 mμ, and $E_{max.}$ was 0.048 (Table 1 and Fig. 1, Curve 3).

No. 10. The solution of $C_6H_5NMe_2$ had a concentration of $3.1 \cdot 10^{-3}$ M. No measurements of the maximum were given at d = 1.0 cm.

2. Investigation of Solutions of p-$CH_3OC_6H_4NMe_2$ in Nitrobenzene (Complex III)

The ratio was 1AK : ∞ BK; BK = $C_6H_5NO_2$ and AK = N,N-dimethyl-p-anisidine.

No. 11. At a concentration of $1.04 \cdot 10^{-3}$ M: $\lambda_{max.}$ 431 mμ, $E_{max.}$ was 0.402 mμ (Table 2).

No. 12. At a concentration of $0.84 \cdot 10^{-4}$ M: $\lambda_{max.}$ was 428.5 mμ, and $E_{max.}$ was 0.060.

However, if one considers that at 428 and 429 mμ only an extremely insignificant cusp is observed, compared with an E of 0.059 at 430, 431 and 432 mμ, then it will be more correct to assume for $\lambda_{max.}$ the value 430 mμ, found by calculation from the half-width of the band of the region from 427 to 433 mμ (Table 2, Fig. 1, Curve 4).

No. 13. We were unable to measure the maximum at a concentration of $6.8 \cdot 10^{-2}$ M and d = 1.0 cm.

3. Investigation of a Solution of p-Dimethylaminostilbene in Nitrobenzene (Complex VI)

The ratio was 1AK : ∞ BK.

No. 14. 4-$Me_2NC_6H_4CH{=}CHC_6H_5$ (AK) was dissolved in nitrobenzene (BK).

The concentration was $0.83 \cdot 10^{-4}$ M; $\lambda_{max.}$ 430 mμ, $E_{max.}$ 0.207 (Table 2, Fig. 4, Curve 2).

TABLE 2

Absorption Coefficients $E = \log I_0/I$

λ mμ	Solution Nos.				
	8, c = 10^{-3}	9, c = $0.95 \cdot 10^{-4}$	11, c = $1.04 \cdot 10^{-3}$	12, c = $0.84 \cdot 10^{-4}$	14, c = $0.83 \cdot 10^{-4}$
400	0.030	0.006	0.096	0.014	0.040
405	–	–	0.098	0.014	0.042
410	0.033	0.007	0.100	0.015	0.043
415	–	0.010	0.143	0.026	0.045
420	0.109	0.025	0.163	0.035	0.062
422	0.140	0.033	–	0.044	–
424	0.171	0.039	–	0.050	–
425	–	–	0.292	–	0.165
426	0.194	0.045	0.312	0.057	–
427	0.199	0.047	0.324	0.058	–
428	0.199	0.048	0.334	0.060	0.205
429	0.200	0.048	0.338	0.060	–
430	0.197	0.047	0.340	0.059	0.207
431	0.192	0.047	0.402	0.059	–
432	0.188	0.045	0.338	0.059	0.202
433	0.182	0.044	0.335	0.058	–
434	0.177	–	0.333	–	0.195
435	0.170	0.042	0.329	0.056	–
436	0.166	–	–	–	0.185
438	0.157	–	–	–	0.178
440	0.149	0.037	0.310	0.051	0.170
445	0.131	0.031	0.288	0.043	–
450	0.112	0.027	0.268	0.039	0.135
455	0.098	0.023	0.247	0.037	–
460	0.082	0.020	0.230	0.035	0.103
470	0.058	0.014	–	0.026	–
480	0.037	0.009	0.157	0.022	0.060
490	0.025	0.005	–	0.016	–
500	0.014	0.002	0.100	0.012	0.033
520	–	–	0.062	0.007	0.020
540	–	–	0.020	0.003	0.012

The yellow color of the solution was appreciably deeper than that of the nitrobenzene itself or of a solution of dimethylaminostilbene in alcohol.

4. Investigation of Solutions with 4-Dimethylaminostilbene and 4-Nitrostilbene (Complex V) in Pyridine

Symbols: AK = $C_6H_5CH=CHC_6H_4NMe_2$-p; BK = $C_6H_5CH=CHC_6H_4NO_2$-p.

No. 15. The BK in pyridine was at a concentration of 10^{-4} M; $\lambda_{max.}$ was 342.5 mμ, as the average of the four values of 341-344 mμ, with the same E of 0.905, and $\epsilon_{max.}$ of 23,000; log $\epsilon_{max.}$ was 4.36 (Fig. 2, Curve 1);

No. 16. The AK in pyridine was at a concentration of 10^{-4} M: $\lambda_{max.}$ was 356 mμ for an $E_{max.}$ of 2.30; $\epsilon_{max.}$ was 9050; log $\epsilon_{max.}$ was 3.96 (Fig. 2, Curve 2).

No. 17. The calculated sum of absorption for [AK + BK] in pyridine was on the basis of No. 15 and 16; and a concentration of 10^{-4} M (Fig. 2): $\lambda_{max.}$ was 355 mμ for $E_{max.}$ of 3.19; $\epsilon_{max.}$ 31,860; log $\epsilon_{max.}$ was 4.50 (Fig. 2, Curve 3).

No. 18. The solution of 1AK : 1BK in pyridine was at a concentration of 10^{-4}M for each compound forming the complex.

The position of the maximum could not be accurately measured for d = 1.0 cm, as a consequence of the strong absorption. The approximate position of the maximum could be calculated from the half-width of the band between 320 and 380 mμ for the same E of 2.7. We found then, that $\lambda_{max.}$ lay at about 350 mμ, which almost coincided with the value calculated for the sum of the compounds taken (cf. Solution No. 17; Fig. 2, Curve 4).

If the determined values of E are compared with the calculated values, then it can be concluded that some interaction is observed between the AK and BK component at a concentration of 10^{-4} M and at a ratio of 1AK : 1BK. The present AK component was thus found to be more active than $C_6H_5NMe_2$.

No. 19. The solution in pyridine (1AK : 1BK) was at a concentration equal to 10^{-3} M for each component. A $\lambda_{max.}$ of 385 mμ at $E_{max.}$ of 2.00 was found; ε 2000; log $\epsilon_{max.}$ was 3.35.

According to the position of the maximum, it can be concluded that the main bulk of the mixture does not enter into complex formation (cf. No. 5 and No. 16). However, by calculation for the sum of the components (No. 17) a bathochromic displacement of $\Delta\lambda_{max.}$ = + 30 mμ, compared with a $\lambda_{max.}$ of 355 mμ, indicated that at concentration equal to 10^{-3} M, and at a molar ratio of the components, complex formation was already considerably greater than at a concentration of 10^{-4} M.

No. 20, and 21. The solutions of p-nitrostilbene and p-dimethylaminostilbene were with a 3-fold excess of one of the components (Fig. 3 and Fig. 2, Curves 5 and 6).

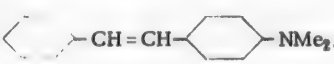
Solution No.	Ratio of components in solution, in moles	$\lambda_{max.}$ in mμ	$E_{max.}$	Concentration in pyridine (M)		Reference solvent in pyridine (M)
				AK	BK	
20	1AK• : 3BK••	438	1.09	0.02	0.06	BK 0.04
21	3AK : 1BK	430	1.86	0.06	0.02	AK 0.04

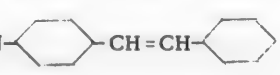
5. Investigation of Solutions of $p\text{-}O_2NC_6H_4NMe_2 + C_6H_5NO_2$ in Pyridine and in Nitrobenzene

No. 22. The p-nitrodimethylamiline in pyridine was at a concentration of 10^{-4}M: $\lambda_{max.}$ 396 mμ at an $E_{max.}$ of 2.00; $\epsilon_{max.}$ was 20,000; log $\epsilon_{max.}$ was 4.30 (see Fig. 1, Curve 5).

No. 23. The p-nitrodimethylaniline in nitrobenzene was at a concentration equal to 10^{-4} M. For the complex [$p\text{-}O_2NC_6H_4NMe_2 + C_6H_5NO_2$] $\lambda_{max.}$ was 420 mμ at an $E_{max.}$ of 0.720, $\epsilon_{max.}$ was 7200, log $\epsilon_{max.}$ was 3.86 (Fig. 1, cf. Curve 6 and Curve 7).

No maximum could be observed for a concentration of 10^{-3} M.

• AK: 

•• BK: 

6. Investigation of Solutions of 4-$O_2NC_6H_4CH{=}CHC_6H_4NMe_2$-4' in Pyridine and in Nitrobenzene

No. 24. The solution in pyridine was at a concentration of 10^{-5} M $\lambda_{max.}$ was 451 mμ; $\epsilon_{max.}$ was 26,900, and log $\epsilon_{max.}$ was 4.43 (Fig. 4, Curve 3).

No. 25. The solution in pyridine at a concentration of 10^{-4} M had a $\lambda_{max.}$ of 450 mμ, and a log $\epsilon_{max.}$ of 4.41.

We obtained the following as the average of the measurements with Solutions No. 24 and 25 with the Beckmann photoelectric spectrophotometer: a $\lambda_{max.}$ of 450.5 mμ, and a log $\epsilon_{max.}$ of 4.42. These figures agree well with P. I. Samokish's data, obtained with a spectrograph by the photographic method: a $\lambda_{max.}$ of 450.5 mμ, and a log $\epsilon_{max.}$ of 4.45 [1]•.

No. 26. No maximum could be accurately measured for a solution in pyridine at a concentration equal to 10^{-2} M. We obtained a $\lambda_{max.}$ of about 455 mμ if we take the average between 450 and 460 mμ at a log $\epsilon_{max.}$ of 3.91. Moreover, the upper part of the curve in the region of the maximum is shifted rather considerably toward the smaller log ϵ values, compared with No. 24 and 25. It is possible that this is a consequence of intermolecular interaction of nitrodimethylaminostilbene itself at higher concentrations. It is necessary to verify these observations because of their importance.

No. 27. The solution in nitrobenzene was at a concentration equal to $0.83 \cdot 10^{-4}$ M.

Two closely-lying maximum of α $\lambda_{max.}$ of 452.5 mμ and β $\lambda_{max.}$ of 448 mμ (at E > 2) were observed. Between the maxima at 449, 450, and 451 mμ there was only an extremely small decrease of E to 2.00.

No. 28. The solution in nitrobenzene was at a concentration equal to $0.83 \cdot 10^{-5}$ M.

Just as for No. 27, two closely-lying maxima were observed: α $\lambda_{max.}$ at 452 mμ ($E_{max.}$ was 0.218, $\epsilon_{max.}$ was 26,170, log $\epsilon_{max.}$ was 4.41), and β $\lambda_{max.}$ was 448 mμ ($E_{max.}$ was 0.218, $\epsilon_{max.}$ was 26,170, log $\epsilon_{max.}$ 4.41).

Between the maxima there was only an extremely small decrease of E to 0.217 (E 26,060, log ϵ 4.416) (Fig. 4, Curve 4).

If the position of the maximum band is determined by the average from the half-width, then it can be assumed that $\lambda_{max.}$ for solutions in nitrobenzene lies at about 450 mμ at concentrations of 10^{-4}-10^{-5} M. No bathochromic displacement of the maximum was observed, compared with the position of the maximum in a solution of pyridine, as it was for p-nitrodimethylaniline (No. 23). In the present case nitrobenzene showed no reaction, and no formation of a complex with nitrobenzene occurred.

SUMMARY

1. The absorption spectrum of a solution of [$C_6H_5NO_2$ + $C_6H_5NMe_2$] in pyridine at concentrations of 10^{-3} and 10^{-4} M almost coincided with the spectrum calculated for the sum of the components, which indicates the almost complete absence of formation of a complex.

The equilibrium AK + BK $\rightleftharpoons$ [AK$\frown$BK] may be shifted toward the complex, using nitrobenzene as the solvent; $\lambda_{max.}$ was 429 mμ.

2. The absorption spectra of 4-nitrostilbene, dimethylaminostilbene and 4-nitro-4'-dimethylaminostilbene in pyridine were measured.

Using a 3-fold excess of one of the components, an increased concentration of 0.02 M, and the differential method for spectroscopy, wer were able to determine the position of the maximum for the complex [$O_2NC_6H_4CH{=}{=}CHC_6H_5$ + $C_6H_5CH{=}CHC_6H_4NMe_2$] in pyridine; $\lambda_{max.}$ was 438 mμ with an excess of the nitro compound and 430 mμ for an excess of the amino compound.

3. For solutions of p-dimethylaminoanisole and p-dimethylaminostilbene in nitrobenzene the position of the maximum was found to be in the region close to 430 mμ.

4. The observation was made that, with an excess of the nitro component (BK), $\lambda_{max.}$ for the complex can lie in the longer wave region than for the corresponding compound with a conjugated system, for example, for the

• It was a Hilger (13 X 18 "Intermediate" Model) spectrograph with a Sheib-Fyuss photometric apparatus with a rotating sector. The intensity of blackening on the spectrogram in the area of the maximum was determined by means of a Zeiss microphotometer.

complex (II) compared with (I), and (V) compared with (VI).

With an excess of the dimethyl amin[illegible] (AK) in solution, a shift of the maximum toward the shorter waves was observed, and in some cases the effect of interaction with the formation of a colored complex was absent. Thus, for a solution of 4-nitrostilbene in dimethyl[illegible] $\lambda_{max.}$ was 358 mμ.

5. A $\lambda_{max.}$ of 429 mμ ($\lambda_{max.}$ in pyridine was 395 mμ) was found for a solution of p-nitrodimethylaniline in nitrobenzene. No change was observed for the position of the maximum for p,p'-nitrodimethylaminostilbene in nitrobenzene (450 mμ), compared with a solution in pyridine.

6. In certain cases the region of absorption of a molecular complex of the (AK + BK) type can lie extremely close (and sometimes even in the longer wave region) to the region of absorption for a compound with a conjugated system of the A – K – B type, which contains the same AK and BK polar systems in the molecule.

The reduction of the energy of excitation as a result of the interaction through exo-forces of two polar-antithetical chromophoric systems in the complex is perhaps extremely close to the effect observed for interaction of the same chromophoric systems through endo-forces in a molecule with a conjugated system.

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Received December 10, 1953

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INVESTIGATION OF COMPLEX COMPOUNDS OF Met[BAr_4]

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In previous works we reported on the results of an investigation of borate-onic compounds. On shaking chloroform solutions of Met[$B(C_6H_5)_4$][1] or Met[BAr_3Ar'][2] with mercury at ordinary temperature, a free-radical transition reaction of one of the anion radicals to mercury occurs, with the formation of diarylmercury. It was shown that for an anion having two different radicals, the breaking away of naphthyl- and p-tolyl radicals chiefly, compared to phenyl, proceeds. The same sequence of breaking away was observed on thermal decomposition of $NH_4[BAr_3Ar']$, i.e., a splitting off of the more electronegative radical took place.

In the present work we attempted to extend the investigation of those types of compounds which will also have aliphatic radicals in the [BR_4] anion, and to study the reactions of the anions, which take place with the breaking away of one radical. Derivatives with alkyl radicals in the anion have been investigated very little as yet. A series of dialkyl and arylalkyl mixed derivatives, which were substituted in the anion, have been described: $Li[B(CH_3)_3C_2H_5]$[3], $Li[BC_6H_5(C_4H_9)_3]$[4], $Li[B(C_6H_5)_3C_4H_9]$[5], and $Li[B(C_6H_5)_3C{\equiv}CC_6H_5]$[6], but they are unstable, and all of them except the last are obtained only in solutions.

We attempted to obtain from $(C_6H_5)_3B$ and CH_3Li or from $(\alpha\text{-}C_{10}H_7)_3B$ and C_2H_5Li the corresponding complex compounds $Li[B(CH_3)(C_6H_5)_3]$ or $Li[BC_2H_5(C_{10}H_7)_3]$. The precipitates obtained by mixing solutions of the indicated components were not very stable, and quickly decomposed on storage in the air. The aqueous solutions of the compounds just obtained gave no precipitates with potassium or ammonium salts. However, on standing of the above-indicated solutions, an increasingly complete separation of precipitates with K and NH_4 cations was initiated. An analysis of the precipitates showed that they consisted of $K[B(C_6H_5)_4]$ and $K[B(C_{10}H_7)_4]$ or the corresponding ammonium derivatives. Thus, it can be assumed that in the solutions, a symmetrization of the $[B(CH_3)(C_6H_5)_3]^-$ and $[B(C_2H_5)(C_{10}H_7)_3]^-$ anions occurs. In this reaction, there is an analogy with the symmetrization of the asymmetrical compounds of trivalent boron. Thus, for example, a mixture of triethylboron and triphenylboron was obtained on attempts to synthesize diethylphenylboron [7].

In work with $K[B(C_6H_5)_4]$, which was very difficultly soluble in water, an interesting peculiarity was observed: the potassium complex was soluble in acetone, the monomethyl ether of ethylene glycol, and in some other solvents. On addition of water to the solution, the solubility increased, reaching a maximum with the addition of approximately 20% water, then the solubility decreased, and with a large excess of water the complex precipitated completely from solution. On heating of solutions of $K[B(C_6H_5)_4]$ in the monoethyl ether of ethylene glycol, a quantitative breaking away of one phenyl radical results, which takes up hydrogen of the solvent, forming benzene. The solution acquires a brown color. On treatment of the solution, the usual decomposition products of triphenylboron – phenyl and diphenylboric acid – are separated by the action of air and water. The reaction probably takes place according to the equation

$$K[B(C_6H_5)_4] + C_2H_5OCH_2CH_2OH \longrightarrow C_6H_6 + (C_6H_5)_3B + C_2H_5OK + CH_3CHO$$

$$(C_6H_5)_3B \xrightarrow{(O)} (C_6H_5)_2BOC_6H_5 \xrightarrow{H_2O} (C_6H_5)_2BOH + C_6H_5OH.$$

The presence of acetaldehyde in the solution was demonstrated by precipitation of the dimedon derivative. A major portion of the aldehyde was resinified by the action of alkali. On heating of solutions of $NH_4[B(C_6H_5)_4]$ in the monoethyl ether of ethylene glycol or in methanol at 100° in a sealed tube, the splitting off of one phenyl group as benzene also results. Ammonia, triphenylboron (by its decomposition products) and triphenylboron ammoniate were found in the solution. In the present case, it is impossible to say whether an analogous reaction proceeds with the solvent as with the potassium derivative, or whether intramolecular decomposition occurs

$$NH_4[B(C_6H_5)_4] \longrightarrow C_6H_6 + NH_3 + B(C_6H_5)_3.$$

Since the breaking away of one radical proceeds for the reaction described, it would be possible to use the reaction for the determination of the stability of the bond of different radicals with boron in the $[BAr_3AR]^-$ anion. For $K[B(C_6H_5)_3Ar]$, where Ar is α-naphthyl or p-tolyl an almost quantitative breaking away of only the Ar-radical results.

A decomposition of the complexes is observed on exposure of their chloroform solutions to ultraviolet light. Solutions of $Li[B(C_6H_5)_4]$ or $K[B(C_6H_5)_4]$ are decomposed with the breaking away of the phenyl radical which, taking up the hydrogen of the solvent, gives benzene, or on dimerization, forms biphenyl. Due to the chlorine of the chloroform, the metals Li or K yield chlorides. This photoreaction of borate-onic compounds has some similarity to the photoreactions of the -onic compounds. Thus, for example, a deamination reaction proceeds on exposure of alcoholic solutions of the diazo salts and, moreover, the resulting radical breaks away the hydrogen of the solvent [8].

Another type of reaction of the breaking away of one radical from an anion proceeds by the action of bromine on the complexes. In the literature we encountered only one indication for reactions of halides with the complexes, namely, the action of iodine on $Li[B(C_6H_5)_3C\equiv CC_6H_5]$, which takes place with the breaking away of the phenylacetylene radical from the anion. We studied the reaction of $K[B(C_6H_5)_4]$ with bromine, which proceeds according to the equation

$$K[B(C_6H_5)_4] + Br_2 \longrightarrow KBr + C_6H_5Br + (C_6H_5)_3B.$$

In the bromination reaction of complex compounds with $[B(C_6H_5)_3Ar]^-$ anion, the same sequence of the breaking away of radicals is observed. Thus, the reaction proceeds smoothly:

$$Li[B(C_6H_5)_3C_6H_4CH_3] + Br_2 \longrightarrow LiBr + CH_3C_6H_4Br + (C_6H_5)_3B.$$

Together with the decomposition of the complex compounds by halides, an attempt was made to use anhydrous ferric chloride in nonaqueous solvents for this purpose. It is known that in an aqueous solution, by the action of the chlorides of metals like Fe^{++}, Co^{++}, Ni^{++}, Mn^{++}, the formation of hydroxides of the metals and benzene occurs [6]:

$$2Li[B(C_6H_5)_4] + MetCl_2 + 6H_2O \longrightarrow Met(OH)_2 + 2LiCl + 2C_6H_5B(OH)_2 + 6C_6H_6.$$

In an ether solution, the reactions of reduction of the chloride of the metal and of formation of biphenyl are observed, which are explained by the decomposition of the $[B(C_6H_5)_4]^-$ anion, losing one electron during the reduction of the metal

$$2Li[B(C_6H_5)_4] + 2CuCl_2 \longrightarrow 2CuCl + 2LiCl + 2(C_6H_5)_3B + C_6H_5C_6H_5.$$

On further reaction with an excess of the complex, cuprous chloride is reduced to the metal.

The reaction of $Li[B(C_6H_5)_4]$ with ferric chloride in an acetone solution, which we studied, proceeded peculiarly: lithium chloride, biphenyl, benzene and phenylboric acid (after treatment of the reaction mixture with water) were formed. The reaction may be represented by the following equations:

$$Li[B(C_6H_5)_4] + 3FeCl_3 \longrightarrow LiCl + C_6H_5BCl_2 + 3FeCl_2 + C_6H_5C_6H_5 + C_6H_5$$
$$C_6H_5 \xrightarrow{\text{acetone}} C_6H_6.$$

The mechanism of this reaction requires further elucidation.

From the examples cited of the decomposition of the $[BR_4]$ anion, it is evident that in the most diverse reactions the same sequence of the breaking away of the radicals from boron is maintained.

EXPERIMENTAL

Lithium triphenylmethylborate $Li[B(C_6H_5)_3CH_3]$. An ether solution of methyllithium, obtained from CH_3I and Li [9], was added slowly to an ether solution of 2.4 g (0.01 mole) of $(C_6H_5)_3B$ in nitrogen. In all, 30 ml of a 0.3 N solution of CH_3Li (~0.01 mole) was introduced. On addition of the organo-Li compound, a slight evolution of heat of the reaction mixture was observed. The solvent was removed, and the viscous substance which formed was quickly transferred to a beaker. The latter was placed in a vacuum-desiccator. Ether was removed from the substance

at low vacuum. On removal of the ether the contents of the beaker were crystallized. The crystalline precipitate quickly decomposed in the air, with the formation of an oily product. An appreciable odor of ether was observed, and a small quantity of biphenyl was separated by the rapid dissolving of the precipitate in water. The aqueous filtrate had an alkaline reaction to litmus.

Fresh aqueous solutions of the resulting complex yielded no precipitate with K- and NH_4- salts. In time, an appreciable separation of the water-insoluble precipitates in both cases was observed. The ammonium derivative was filtered off, dried and analyzed for its nitrogen content. The latter corresponded to $NH_4[B(C_6H_5)_4]$.

Found %: N 4.33. $C_{24}H_{24}BN$. Calculated %: N 4.16.

Lithium trinaphthylethylborate $Li[B(C_{10}H_7)_3C_2H_5]$. A 1.15 N solution of C_2H_5Li [10] was added slowly to a solution of 5.54 g (0.01 mole) of $(C_{10}H_7)_3B \cdot 2C_6H_6$ in 50 ml of anhydrous ether in a current of nitrogen. In all, 9 ml of a benzene solution of ethyllithium (free of LiBr) was introduced. The ether in the reaction flask boiled up vigorously on addition of the ethyllithium. The mixture was allowed to stand in an atmosphere of nitrogen for several hours. Then the white precipitate which came down was filtered off, washed with benzene and dried in a vacuum-desiccator for 2 hours at 5 mm pressure. 2.5 g of the precipitate was obtained. The precipitate decomposed in the air. It dissolved well in water with a slight turbidity of the solution. An aqueous solution of the resulting compound at first gave no precipitate formation with a KCl and NH_4Cl solution. The formation of water-insoluble, white precipitates with KCl and NH_4Cl was observed after several hours of standing of the solutions. The ammonium derivative was filtered off, washed carefully with water and dried in a vacuum-desiccator. The analytical determination of nitrogen in the compound corresponded to the presence of an NH_4-complex with four naphthyl groups in its anion.

Found %: N 2.78. $C_{40}H_{32}BN$. Calculated %: N 2.61.

Reaction of $K[B(C_6H_5)_4]$ with the monoethyl ether of ethylene glycol. 5 g (0.014 mole) of potassium tetraphenylborate was dissolved in a mixture of 80 ml of the monoethyl ether of ethylene glycol and 20 ml of water. The resulting clear solution was heated for 5-7 hours in a flask with a reflux condenser. At the end of the heating, the mixture was a dark-brown color and had an alkaline reaction to litmus. After the heating, 50 ml of water and 5 ml of 2% alkali were added to the reaction flask, and the benzene which separated was steam-distilled. 1.3 ml (1.04 g) of benzene separated, which amounted to 94% of the theoretical, from the calculation for the breaking away of one phenyl radical from the anion of the complex. The benzene was nitrated with m-dinitrobenzene with a m.p. of 90°. A test of a mixture with pure m-dinitrobenzene gave no melting point depression.

After separation of the benzene, acetaldehyde was determined in the water residue as the dimedon derivative with a m.p. of 140°. A test sample of a mixture with the derivative obtained for pure acetaldehyde melted without a melting point depression.

After removal of the benzene the alkaline residue was acidified with sulfuric acid to an acid reaction to Congo, and was again steam-distilled. Phenol was observed in the water residue. By the action of bromine water, a bromination product of phenol, tribromophenol, was separated in the quantity of 2 g, with a m.p. of 93° (from alcohol), without a depression with the pure substance. Considering that 1 mole of phenol is formed by the oxidation of 1 mole of triphenylboron, the resulting yield of the former, based on the quantity of tribromophenol, amounted to 60% of the theoretical.

After steam-distillation of the phenol, an oil with the characteristic odor of diphenylboric acid, which melted in hot water, remained in the flask. The resulting oil was not investigated closely.

No potassium tetraphenylboron was observed after the reaction. Thus, the reaction went to completion.

Reaction of $NH_4[B(C_6H_5)_4]$ with the monoethyl ether of ethylene glycol. 3.36 g (0.01 mole) of the complex in 75 ml of the monoethyl ether of ethylene glycol and 25 ml of water was heated for 2 hours at boiling. No evolution of gaseous NH_3 was observed. The solvent was removed. The first 20 ml of the distillate was diluted with water. 1 ml (0.8 g) of benzene, corresponding to the breaking away of one phenyl group, was formed.

The presence of phenol in the water layer was demonstrated qualitatively by its reaction with bromine. The tribromophenol (0.4 g) which separated had a m.p. of 93°. In the flask after steam-distillation was an oil which had the odor of diphenylboric acid.

Reaction of $NH_4[B(C_6H_5)_4]$ with methyl alcohol. 3.36 g (0.01 mole) of ammonium tetraphenylborate was heated with 20 ml of anhydrous methyl alcohol in a sealed tube in a boiling water bath for 5 hours. At the end of the heating, the precipitate had disappeared, and a clear solution of a yellowish color had formed. The tube was opened and the liquid volume (25 ml) was measured; 1 ml of solution was removed, in which the ammonia content was

determined by titration with hydrochloric acid (2.4 ml of 0.1 N HCl was consumed by 1 ml of solution). The total quantity of ammonia liberated during the reaction was 0.102 g (0.006 mole), which corresponds to a 60% decomposition of the complex. The solvent was distilled. On dilution of the first 10 ml of the solution, 0.8 g of benzene (theoretical yield, by calculation for one phenyl group) was separated.

After removal of the solvent the residue was washed with hot water, dried and weighed. It melted at 212-214° (sintering began at 203°) after recrystallization from hot benzene. The nitrogen content corresponded to triphenylboron ammoniate.

Found %: N 5.30, 5.59. $C_{18}H_{18}BN$. Calculated %: N 5.42.

1 g of the ammoniate was separated, which corresponds to a 38% decomposition of the complex to benzene and the ammoniate.

After separation of the ammoniate, phenol was found in the aqueous filtrate, and identified as the tribromophenol with a m.p. of 92°. 1.9 g of the product was obtained.

The reaction of $K[B(C_6H_5)_3C_{10}H_7]$ with the monoethyl ether of ethylene glycol. 3 g (0.006 mole) of potassium triphenylnaphthylborate was dissolved in 100 ml of the monoethyl ether of ethylene glycol, and was heated at boiling for 2 hours. At the end of the heating the dark-brown solution had an alkaline reaction to litmus. The solvent was distilled. From the residue after steam-distillation, 0.6 g (0.005 mole) of naphthalene, with a m.p. of 80°, was separated. The presence of phenol in the water residue was demonstrated by its reaction with bromine. 0.3 g of tribromophenol with a m.p. of 92° was separated, without a melting point depression in a test of a mixture with the pure substance.

Reaction of $NH_4[B(C_6H_5)_3C_{10}H_7]$ with the monoethyl ether of ethylene glycol. 3 g (0.008 mole) of ammonium triphenylnaphthylborate was dissolved in a mixture of 75 ml of the monoethyl ether of ethylene glycol and 25 ml of water. The mixture was heated for 5 hours in a flask with a reflux condenser. At the end of the heating, the solution in the flask had acquired a brown color. After removal of most of the monoethyl ether of ethylene glycol and the water, the residue was steam-distilled. 1 g (0.0077 mole) of naphthalene with a m.p. of 80° was obtained, without a depression with pure naphthalene.

In the flask (after removal of the naphthalene) on cooling, a crystalline precipitate which was highly soluble in methanol, separated. The precipitate, recrystallized from benzene and washed with anhydrous ether, consisted of 1.1 g (0.0042 mole) of light-weight, snow-white needles with a m.p. of 212-214°. An analysis confirmed the formation of triphenylboron ammoniate.

Found %: N 5.54. $C_{18}H_{18}BN$: Calculated %: N 5.42.

After separation of the ammoniate, phenol was determined qualitatively in the aqueous filtrate as tribromophenol with a m.p. of 93°.

Reaction of $K[B(C_6H_5)_3C_6H_4CH_3]$ with the monoethyl ether of ethylene glycol. A solution of 3.33 g (0.009 mole) of potassium triphenyltolylborate in a mixture of 70 ml of the monoethyl ether of ethylene glycol and 30 ml of water, was heated for 6 hours in a flask with a reflux condenser. The solvent was removed. The first portion of the distillate was diluted with water, and 0.8 g (0.0087 mole), or 96% of the theoretical yield of toluene, was separated. For identification, the toluene was oxidized by an alkaline solution of permanganate. The resulting benzoic acid melted at 121° without a depression with known, pure benzoic acid.

After removal of the solvent and toluene, phenol was determined in the reaction mixture (by conversion to tribromophenol with a m.p. of 93°).

Reaction of $K[B(C_{10}H_7)_3C_6H_5]$ with the monoethyl ether of ethylene glycol. 4.8 g (0.0095 mole) of the complex was dissolved in a mixture of 80 ml of the monoethyl ether of ethylene glycol and 20 ml of water. The mixture was heated at boiling for 4 hours. At the end of the heating, the solution was a dark-brown color. The medium was alkaline. By steam-distillation, 2.5 g (0.0195 mole) of naphthalene with a m.p. of 80° was separated from the reaction mixture, without a depression with the pure substance which corresponded to the breaking away of two naphthyl groups.

The aqueous solution in the flask (after separation of the naphthalene) was evaporated and acidified with sulfuric acid. On cooling, a small quantity of phenylboric acid was separated. The latter was converted to the anhydride by long drying in the air. A test of a mixture with the anhydride of phenylboric acid gave no depression (190°).

Reaction of $K[B(C_6H_5)_4]$ with bromine. A solution of bromine in methanol was introduced dropwise into a suspension of 3.5 g (0.01 mole) of potassium tetraphenylborate in 25 ml of anhydrous methanol, with stirring. In proportion to the addition of bromine, the precipitate of the complex dissolved, with simultaneous disappearance of the bromine color. In all, 8 ml of a 1.25 M solution of bromine, or 1.6 g of bromine (0.01 mole) was introduced. The alcohol was removed. A layer of bromobenzene in a quantity of 1.5 g (0.01 mole) separated on dilution of the residue with water. For identification, the bromobenzene was nitrated to 1,2,4-bromodinitrobenzene. A test sample of a mixture of the resulting nitro product with pure 1,2,4-bromodinitrobenzene had a m.p. of 59°.

After removal of the alcohol and the bromobenzene the residue was steam-distilled. 1 g (0.0065 mole) of biphenyl with a m.p. of 68° was distilled. A test sample of a mixture with pure biphenyl had a m.p. of 70°. The aqueous solution from the steam-distillation flask was evaporated in vacuo at 50-60°. On cooling, 1 g (0.0083 mole) of phenylboric acid crystallized. Its m.p. was 190° (if heating of the capillary was begun in cold sulfuric acid); on the heated sulfuric acid bath it melted with pure phenylboric acid at 214-216° without a depression.

Reaction of $Li[B(C_6H_5)_3C_6H_4CH_3]$ with bromine. A 0.16 M solution of bromine was introduced dropwise into a solution of 2.6 g (0.0077 mole) of lithium triphenyltolylborate in 50 ml of water. The bromine was added until the appearance of a pale-yellow color. In all, 45 ml of bromine water, or 1.2 g (0.0075 mole) of bromine was added. p-Bromotoluene was steam-distilled from the reaction flask. p-Bromobenzoic acid, m.p. 251°, was obtained by the oxidation of p bromotoluene with permanganate. A test sample of a mixture with pure p-bromobenzoic acid melted without a depression. In all, 1.1 g (0.006 mole) of p-bromotoluene separated, which amounted to 80% of the theoretical yield. A small quantity of biphenyl with a m.p. of 70° separated on distillation of the bromotoluene. After separation of the bromotoluene and biphenyl, the presence of a dark, viscous liquid with the characteristic odor of diphenylboric acid was observed in the residue.

Photoreaction of $K[B(C_6H_5)_4]$ with chloroform. 3.5 g of potassium tetraphenylborate and 30 ml of chloroform was exposed for 100 hours. The precipitate of the unreacted complex was filtered off. The chloroform was removed. In the distillate, 0.2 g of m-dinitrobenzene with a m.p. of 90° was separated by nitration, and a test sample of a mixture with pure m-dinitrobenzene melted without a depression. After removal of the chloroform the residue was steam-distilled. 0.3 g of biphenyl with a m.p. of 70°, without a depression with the pure substance, separated. The presence of phenol was demonstrated in the aqueous distillate by its reaction with bromine. KCl was found in the precipitate of the unreacted complex.

Reaction of $K[B(C_6H_5)_4]$ with $FeCl_3$. A solution of 7.3 g (0.045 mole) of anhydrous $FeCl_3$ in 20 ml of acetone was added rapidly to a solution of 4 g (0.011 mole) of potassium tetraphenylborate in 100 ml of dry acetone. The mixture was heated on the water bath for 30 minutes. Then the solvent was distilled off. On dilution of the distillate with water, drops of benzene separated on the surface, which were extracted with carbon tetrachloride and nitrated. 1.2 g of m-dinitrobenzene (64% on the basis of one phenyl), with a m.p. of 90°, separated. A test sample of a mixture with the pure nitro product had a m.p. of 90°.

After separation of the acetone and benzene the residue was steam-distilled. 1.3 g of biphenyl, 75.5% by calculation for 2 phenyls, m.p. of 70°, distilled. A test sample of a mixture with pure biphenyl melted at 70°. After the steam-distillation there was a strongly acid reaction in the residue. The reaction for Fe^{++} was positive. In the aqueous filtrate Fe^{+++} was precipitated as the hydroxide and filtered off. The filtrate was evaporated in vacuo (50-60°) and acidified with H_2SO_4 to an acid reaction to Congo. On cooling, white crystals of phenylboric acid precipitated. Their m.p. was 190° (in a heated bath).

SUMMARY

1. Lithium ethyltriphenylborate and lithium methyltrinaphthylborate, obtained by the usual method in aqueous solutions, were symmetrized. The fresh solutions gave no precipitates with K and NH_4 cations; on standing of the solutions, difficultly soluble tetraphenylborates or tetranaphthylborates of potassium and ammonia formed.

2. On heating of the complex compounds in a solution of the monoethyl ether of ethylene glycol, their decomposition took place with the breaking away of one radical from the anion which, taking up hydrogen from the solvent, gave a hydrocarbon. It was shown that, compared with phenyl, p-tolyl- or α-naphthyl- radicals broke away first on decomposition of the $[B(C_6H_5)_3C_6H_4CH_3]$ or $[B(C_6H_5)_3C_{10}H_7]$ anions.

3. On exposure of chloroform solutions of the tetraphenylborates to ultraviolet light, the breaking away of the phenyl radical resulted which, taking up hydrogen from the chloroform, formed benzene.

4. Bromobenzene, triphenylboron and potassium bromide were formed by the action of bromine on potassium

tetraphenylborate. On reaction of bromine with lithium triphenyltolylborate, the tolyl radical broke away.

5. By the action of ferric chloride on an acetone solution of lithium tetraphenylborate, lithium chloride, biphenyl, phenylboric acid (after treatment with water) and benzene formed, due to the breaking away of hydrogen from acetone by the phenyl radical.

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Received February 9, 1954.

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STUDY OF THE REACTION RATE OF THE FORMATION OF l-ASCORBIC ACID FROM THE HYDRATE OF DIACETONE-2-KETO-l-GULONIC ACID IN AN AQUEOUS MEDIUM

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The conversion of 2-keto-l-gulonic acid and its acetonized derivative, the hydrate of diacetone-2-keto-l-gulonic acid, to l-ascorbic acid, is the subject of numerous investigations. The reaction may be carried out under different conditions: with and without catalysts, without a solvent, in an aqueous solution, in a medium of organic solvents, etc. (reviews [1, 2]). In spite of the presence of numerous works and patents in this field, the theory of the process is still inadequately developed with respect to the conditions of carrying out the reaction. Berezovsky and Strelchunas [3] investigated in detail the course of the reaction in a medium of an inert organic solvent, under the influence of hydrogen chloride in the presence of alcohols, and interpreted the chemism of the process.

There is much less data on the course of the reaction in an aqueous medium. Yet Reichstein and Grüssner [4] found that on heating with water at 100°, 12.7% of the 2-keto-l-gulonic acid was converted to ascorbic acid after 2 hours. The reaction proceeded with a higher yield at 120-140° under pressure [5, 6].

Reichstein and Grüssner showed that the reaction is accelerated considerably by the addition of acids; a 27% yield of ascorbic acid was obtained after 4 hours in a 0.2 N solution of HCl at 100°. They found that on prolonged action, hydrochloric acid decomposed the ascorbic acid [4]. Hirst and his coworkers showed that furaldehyde and its polymers are formed by the decomposition of ascorbic acid under these conditions [7]. There are numerous patents on the production of l-ascorbic acid in the presence of different acids (review [2]).

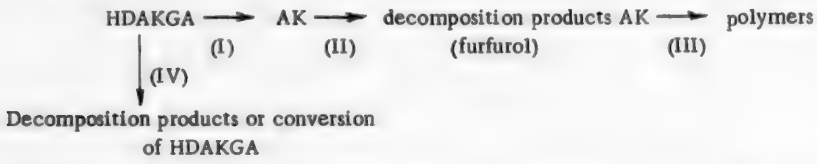
The kinetics of the conversion of 2-keto-l-gulonic acid to ascorbic acid in an aqueous medium was studied in detail by Regna and Caldwell [8]. The reaction was investigated under the following conditions: the HCl concentration in the reaction mixture amounted to 5 moles/liter, the initial concentration of 2-keto-l-gulonic acid amounted to 0.05 mole/liter, and the temperature was 59.9° and 69.9° (± 0.02°). The previously established scheme of the course of the process studied was confirmed kinetically by Regna and Caldwell:

$$\text{2-keto-l-gulonic acid} \xrightarrow[(I)]{K_1} \text{l-ascorbic acid} \xrightarrow[(II)]{K_2} \text{decomposition products of l-ascorbic acid} \xrightarrow[(III)]{K_3} \text{polymers}$$

They determined the rate constants of the reactions of formation of l-ascorbic acid (K_1) and of its decomposition (K_2) as consecutive reactions of the first order ($K_1 = 2.5 \cdot 10^{-3}$ and $8.2 \cdot 10^{-3}$, $K_2 = 4.9 \cdot 10^{-4}$ and $14.1 \cdot 10^{-4}$ at 59.9 and 69.9°, respectively. On the basis of the values of K_1 and K_2 the potential maximum yields of l-ascorbic acid were calculated, which were confirmed experimentally. At 59.9° the maximum yield amounted to 67.6%, and at 69.9° it was 69.9% of the theoretically possible yield.

The study of the reaction rate of the formation of l-ascorbic acid (AA), by heating the hydrate of diacetone-2-keto-l-gulonic acid (HDAKGA) with concentrated hydrochloric acid, was the problem of the present work. We studied systems, unlike Regna and Caldwell's experiments, with high organic acid contents (2-2.5 moles/liter), but with a similar hydrogen chloride content in the system (~5 moles/liter); moreover, our systems contained acetone, which formed on hydrolysis of the HDAKGA. This presented the possibility of judging whether a change of composition of the mixture (increased organic acids content, presence of acetone, decreased quantity of water, with the same catalyst content), and whether replacement of 2-keto-l-gulonic acid by its diacetone derivative, would affect the rate of the process. Since it is known that in an acid medium the cleavage of acetone and the formation of 2-keto-l-gulonic acid proceeds extremely rapidly [4], this latter condition could seem unessential at first sight.

At the same time, kinetic data would enable us to judge the mechanism of the reaction, to establish the presence or absence of parallel side reactions of the decomposition of HDAKGA or of its conversion to other products (IV), under the conditions studied:



The investigation included the conduction of two series of experiments: the rate of accumulation of AA in the reaction mixture, and parallel with it, the rate of decomposition of AA, were determined under similar conditions. The constants of the reaction of formation of AA (k_1) and the decomposition of AA (k_2) were calculated on the basis of the data obtained. This method, used by Regna and Caldwell before us, was the most logical, since there was no suitable method for direct determination of the 2-keto-l-gulonic acid in the reaction mixtures.

EXPERIMENTAL*

General Method. Measurement of the reaction rates was carried out by heating samples of the reaction mixtures with definite ratios of components in sealed test tubes, which were placed in a water thermostat with an accuracy of temperature regulation of ±0.1°. After a definite time, the tubes were removed from the thermostat and cooled with cold water, after which the determination of the ascorbic acid content was carried out at once by titration with iodine, with the use of starch as an indicator. The investigation was carried out at 60 and at 70° (±0.1°), with different ratios between the quantities of the hydrate of diacetone-2-keto-l-gulonic acid (or ascorbic acid) and the hydrochloric acid concentration. An experiment was carried out at 50° for comparison.

Preparation of the reaction mixtures. HDAKGA – hydrochloric acid mixtures. I. HDAKGA: hydrochloric acid ratio = 1.575 g of HDAKGA per 1 ml of concentrated hydrochloric acid (2.06 moles of HCl per mole of HDAKGA). The hydrogen chloride content in this mixture amounted to ~4.9 moles per 1 liter of the mixture.

II. HDAKGA: hydrochloric acid ratio = 2.39 g of HDAKGA per 1 ml of concentrated hydrochloric acid (1.36 moles of HCl per 1 mole of HDAKGA). The hydrogen chloride content in the reaction mixture amounted to ~3.7 moles per 1 liter of the mixture.

AA – hydrochloric acid – acetone mixtures. Mixtures for determination of k_2 (the rate constant of the decomposition of ascorbic acid) were prepared by mixing weighed portions of AA with acetone and concentrated hydrochloric acid. The acetone was added in a quantity of 2 moles per 1 mole of AA (according to the equation of the hydrolysis reaction of HDAKGA); hydrochloric acid was added in the same ratios, at which it occurred in mixtures with equivalent quantities of HDAKGA.

Starting materials: the hydrate of diacetone-2-keto-l-gulonic acid had a content of 92.4%, based on the anhydrous substance, or 98.5% based on the hydrated molecule. Recrystallized, medicinal l-ascorbic acid contained 99.2%, by iodine. The chemically pure hydrochloric acid contained 11.15 moles/liter of HCl.

Calculation of the reaction rate constants. Calculation of k_2, the rate constant of the decomposition of AA, was made by the usual formula of a first order reaction:

$$k_2 = \frac{2.303}{t} \log \frac{C_0}{C} . \qquad (1)$$

For calculation of k_1, the rate of formation of AK, it is possible to use Formula (2), obtained by transformation of the Rakovsky formula for the determination of the content of the intermediate substance in a consecutive reaction of the first order [9, 10], which is identical with the formula used by Regna and Caldwell [8].

$$k_1 = -\frac{1}{0.4343\, t} \log \left[e^{-k_2 t} - \frac{b}{a_0} \frac{k_1 - k_2}{k_1} \right] . \qquad (2)$$

* M. F. Galina and M. P. Benyamin participated in conduction of the experimental part of the work.

Since, according to our data $k_1 \gg k_2$ (by approximately 100 times), we calculated the value of k_1 by simplified Formula (3)

$$k_1 = -\frac{\log\left[e^{-k_2 t} - \frac{b}{a_0}\right]}{0.4343\,t} \qquad (3)$$

where a_0 is the content of the initial substance (HDAKGA) and b is the content of ascorbic acid at time t.

The maximum possible yield of AA was calculated by the formula [8, 10],

$$\left(\frac{b}{a_0}\right)_{max.} = \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1 - k_2}} \qquad (4)$$

The time necessary for attainment of the maximum yield $t_{max.}$ [9], was determined by the formula

$$t_{max.} = \frac{\ln \frac{k_1}{k_2}}{k_1 - k_2} \qquad (5)$$

Discussion of Results

The experimental data on the determination of the AA content in reaction mixtures, in relation to the time at different temperatures and ratios of components, are cited in Figs. 1 and 2. As a result of the fact that the decomposition of AA proceeded to a negligible extent under the conditions studied, the curves of Fig. 2 approximate straight lines.

TABLE 1

Time (in min.)	$k_1 \cdot 10^2$ at 60° (HCl: HDAKGA = 1.36	Time (in min.)	$k_2 \cdot 10^4$ at 60° (HCl: AA = 1.36)
60	1.1, 1.1	300	1.3, 1.0
90	0.9, 0.9	360	0.8, 1.1
120	0.9, 1.1	480	1.2, 0.6
150	1.2, 1.0	540	0.9, 1.0
180	0.9, 0.9	600	0.8 —
210	0.8, 1.0		
240	0.9, 0.9		

On the basis of the experimental data, the values of the constants of the reaction of formation of AA (k_1) and of the reaction of its decomposition (k_2), were calculated by Formulas (1) and (3) at 60 and 70°. The values of k_1 and k_2 were characterized by satisfactory constancy over the entire time interval, from the beginning of the reaction until the attainment of the maximum yield. A scattering of the values of k_1 and k_2 was observed in parallel experiments, and in experiments with different period of heating which can be explained by the viscous consistency of the reaction mixtures. Data illustrating the resulting values of k_1 and k_2 for two parallel experiments are cited in Table 1.

TABLE 2

Temperature	Initial molar ratio of $\frac{HCl}{HDAKGA}$ (or $\frac{HCl}{AA}$)	Average value of $k_1 \cdot 10^2$	Average value of $k_2 \cdot 10^4$	Calculated maximum yield of AA (in %)	Calculated time of attainment of the maximum yield (min.)
60°	2.06	1.2	1.5	95.0	342
60	1.36	1.0	0.9	95.9	468
70	2.06	2.7	6.4	91.5	136

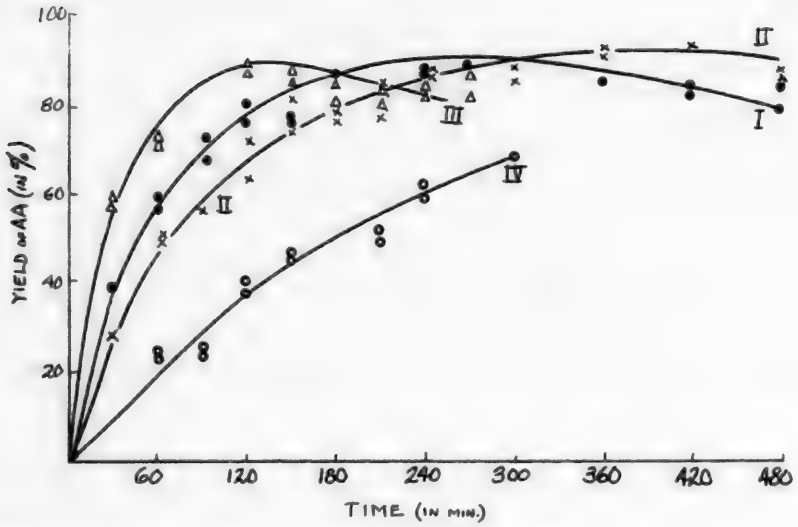


Fig. 1. Relation of ascorbic acid yield to the temperature and composition of the mixture.
A) Yield of AA (in %); B) time (in min.).
I) 60°, 2.06 moles HCl per 1 mole of HDAKGA; II) 60°, 1.36 moles of HCl per 1 mole of HDAKGA; III) 70°, 206 moles of HCl per 1 mole of HDAKGA; IV) 50°, 1.36 mole of HCl per 1 mole of HDAKGA.

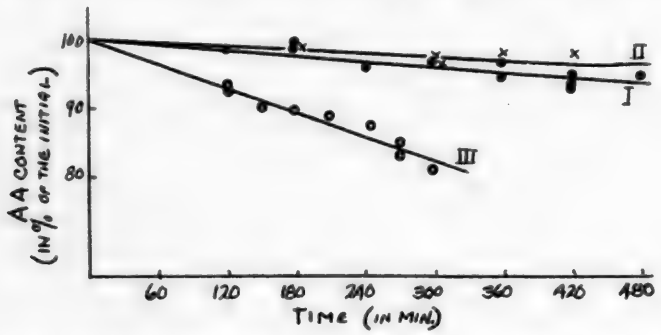


Fig. 2. Relation of the rate of decomposition of ascorbic acid to the temperature and composition of the mixture.
A) AA content (in % of the initial); B) time (in min.).
I) 60°, 2.06 moles of HCl, 2 moles of acetone per 1 mole of AA; II) 60°, 1.36 moles of HCl, 2 moles of acetone per 1 mole of AA; III) 70°, 2.06 moles of HCl, 2 moles of acetone per 1 mole AA.

On the basis of the resulting values of k_1 and k_2, the maximum yields of AA (in molar percentages of the initial quantity of HDAKGA) and the time necessary for attainment of the maximum yield ($t_{max.}$) were calculated. The data obtained are cited in Table 2.

It is seen from a comparison of the data of Table 2 and Fig. 1 that the calculated values of the maximum yield of AA and the times of attainment of the maximum yield agree with those found experimentally. Hence, it is evident that the constant k_1, found for the quantity of AA which formed and calculated by the Rakovsky formula, correctly express the course of the reaction. Therefore, the process is a consecutive reaction of the first order under the conditions studied. It can be predicted on the basis of the data obtained, that parallel reactions of decomposition of HDAKGA will not take place in practice.

Under the conditions investigated, the decomposition of ascorbic acid increases sharply with an increase of temperature (by about 4 times in the interval from 60 to 70°). The rate of conversion of HDAKGA to AA also increased, but to a smaller degree (approximately by 2 times in the temperature interval indicated); therefore, with

an increase of temperature, the overall process of accumulation of ascorbic acid in the reaction mixture has a tendency to decrease.

In connection with this, and also in connection with the increase of the absolute rate of the reaction, the time required for attainment of the maximum yield decreases sharply with an increase of temperature (approximately from 6 hours at 60° to 2 hours at 70°). The rate of the process depends also on the quantity of hydrochloric acid in the mixture. The rate of decomposition of ascorbic acid decreases somewhat with a decrease of the quantity of hydrochloric acid supplied per unit weight of HDAKGA, under the conditions studied. At the same time, the rate of conversion of HDAKGA to AA drops, which can be explained by the decrease of the hydrogen chloride concentration in the reaction mixture. This fact appears to be useful in the increase of the time necessary for attainment of the maximum yield. Moreover, it is necessary to note that an increase of duration and temperature of the process is accompanied by the formation of a considerable quantity of resin.

A comparison of the values of k_1 and k_2, cited in Table 2 with Regna and Caldwell's data indicated above, showed that under the conditions which we studied, the value of k_1 was 3-5 times larger and the value of k_2 was smaller by a factor of 2-3. This can be explained by a consideration of the different composition of the reaction mixtures cited above, particularly by the small quantity of water in the mixtures which we studied. However, it is not excluded that the rates of conversion of the hydrate of diacetone-2-keto-l-gulonic acid, and of the same 2-keto-l-gulonic acid to ascorbic acid may be different.

SUMMARY

1. The reaction rate of production of l-ascorbic acid from the hydrate of diacetone-2-keto-l-gulonic acid by heating it with concentrated hydrochloric acid was investigated.

2. The rate constants of the formation and of the decomposition of l-ascorbic acid, the maximum potential yields, and the times necessary for attainment of the maximum yield were determined at 60 and 70°.

3. It was shown that a monomolecular consecutive reaction takes place under the conditions studied.

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Received March 21, 1954.

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EFFECT OF METALLIC IONS ON THE PROPERTIES OF ETHYLCELLULOSE

III. RELATION OF THE ELASTO-PLASTIC CHARACTERISTIC OF ETHYLCELLULOSE GELS TO THE SODIUM ION CONTENT IN THEM

S. A. Glikman, O. G. Efremova and V. M. Averyanova

In our previous reports [1] it was shown that the introduction of calcium and iron compounds into ethylcellulose led to an increase of the viscosity of its solutions in non-polar solvents, and led to an increase of all the elasto-plastic properties of its gels. Moreover, very small quantities of these metals, of the order of a hundredth of a per cent by weight of the ethylcellulose, which corresponds to one metal ion per ten monomeric links (glucose radicals), had a strong effect. It is known [2] that usually a small number of carboxyl groups are included in the molecules of industrial samples of ethylcellulose. Apparently, multivalent cations replacing hydrogen in these groups, are bound between the ethylcellulose molecules by an ionic bond, the energy of which is much greater than that of the hydrogen bond. With a relatively small number of ionic bonds forming, of the order of one per molecule of ethylcellulose, the increase of intermolecular cohesion does not lead to an essential change of the structure of the ethylcellulose solutions, even in non-polar solvents; the true solution state is retained, but the average degree of association of the high-polymer molecules increases. In gels where, instead of labile equilibrium associates, there exists a permanent network of polymer molecules connected between themselves at relatively few points, multivalent metallic ions increase the number and stability of these bonds.

There is little information in the literature on the effect of univalent metallic ions on the properties of the cellulose esters; moreover, the results obtained by different authors are contradictory. Thus, for example, Drinberg [3] observed a strong decrease of the viscosity of nitrocellulose and acetylcellulose solutions on introduction of sodium acetate and palmitate. Meanwhile, Glickman, Mindlin, Guseva and Zeldovich [4] showed that treatment of nitrocellulose by solutions of sodium carbonate led to an increase of the viscosity of its solutions. Relative to ethylcellulose, Evans and Spurlin [2] found that treatment with sodium carbonate led to an increase of the viscosity of its benzene solutions.

Although sodium is an inevitable component of the ash of industrial ethycellulose samples, its effect on the mechanical properties of ethylcellulose and the gels formed by it have not been studied until now.

Objects of investigation and their preparation. Three samples of ethylcellulose, the characteristics of which are cited in Table 1, served as the material for our investigation. Samples 348 and 424 were not studied in the original condition. They were partially decalcified by repeated reprecipitation from acetone-water solutions containing 0.2% HCl, followed by a careful washing out of the Cl^- ions. The ash obtained after combustion of the decalcified preparations contained chiefly SiO_2 and traces of iron and sodium.

TABLE 1

Characteristics of Ethylcellulose Samples

Sample	Ethoxyl number (in %)	Ash content (in %)		Intrinsic viscosity [η] in a mixture of alcohol and benzene	K'
		in original preparation	after treatment		
224	48.0	0.27	–	1.74	0.65
348	46.5	0.36	0.09	2.14	0.48
424	46.4	0.40	0.18	1.66	0.29

For introduction of sodium ions into an 8% solution of ethylcellulose in acetone, a 2% aqueous solution of NaOH was added in such a quantity that the sodium content amounted to 0.1% by weight of the ethylcellulose. The

solution was left for 12 hours, during which from time to time it was stirred. Then the ethylcellulose was precipitated from the solution by distilled water, the precipitate was filtered off, and the filtrate was evaporated in vacuo at 60°. After evaporation the precipitate was added to the main precipitate and dried to constant weight at 100°. This relieved us of the necessity of controlling the quantity of sodium introduced, since the addition remained completely in the preparation.

Sample 224 and pre-decalcified samples 348 and 424 were subjected to such a treatment. For evaluation of the effect of sodium ions, the preparations thus obtained were compared with those reprecipitated from acetone solutions by distilled water, and Sample 348 was also compared with the preparation treated with a $Ca(OH)_2$ solution by a similar method.

The data on the metallic ion contents in the samples are cited in Table 2.

Viscosity of the dilute solutions. We determined the concentration dependence of the viscosity of solutions of ethylcellulose in a mixture of alcohol with benzene (1 : 4) (Sample 348), and in a mixture of alcohol and toluene (1 : 4) (Sample 424). A viscometer of the standard suspended Ubellohde type was used for determination of the viscosity. The determinations were carried out at a constant temperature (20° ± 0.01° for solutions of 424 and 25° ± 0.01° for solutions of 348). The resulting data are presented in Fig. 1.

TABLE 2

Sample	Ash content (in %)	Content of metals by weight of ethylcellulose (in %)		
		Na	Ca	Fe
224 (original)	0.27	not determined	0.090	0.030
224, treated with $Ca(OH)_2$	0.37	not determined	0.190	0.030
224, treated with NaOH	0.37	0.10 introduced	0.090	0.030
348, decalcified	0.09	traces	0.001	0.007
348, treated with $Ca(OH)_2$	0.19	traces	0.100	0.007
348, treated with NaOH	0.19	0.10	0.001	0.007
424, decalcified	0.18	traces	traces	traces
424, treated with NaOH	0.28	0.10	traces	traces

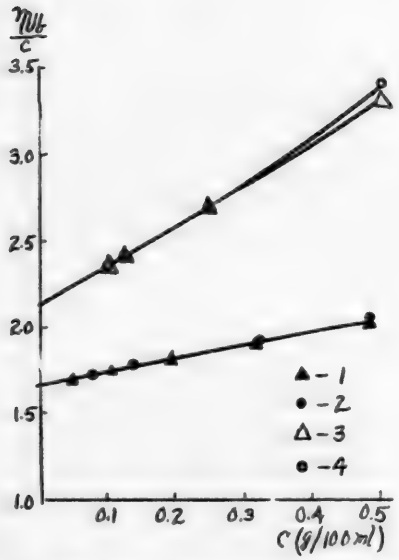


Fig. 1. Effect of treatment with alkali on the viscosity of solutions of ethylcellulose in a mixture of alcohol and benzene.
1) Sample 424, treated with NaOH; 2) sample 424, decalcified; 3) sample 348, treated with NaOH; 4) sample 348, decalcified.

It is evident from the figure that the introduction of small quantities of sodium into the composition of the ethylcellulose was not reflected by the viscosities of its dilute solutions (0.5% and less) in both mixtures of solvents studied. The values of the intrinsic viscosity and the values of the constants K' also remained unchanged. These results agree with those which we obtained earlier [1] relative to the effect of Ca^{++} ions on the viscosity of solutions of ethylcellulose in a mixture of alcohol and benzene. Obviously, here also the polar solvent of alcohols, highly solvating the carboxyl groups of ethylcellulose, screens them, inhibiting intermolecular interaction.

The elasto-plastic properties of the gels. 8 and 10% gels formed by ethylcellulose with dibutylphthalate served as the object of our investigation. We studied five fundamental characteristics, the meaning of which Rebinder [5] defined as follows:

1. P_k is the elastic limit, i.e., the minimum shear stress at which plastic deformation arises.

2. E_1 is the initial (conditionally-instantaneous) modulus of elasticity. $E_1 = \frac{P}{E_0}$, where P is the shear stress and E_0 is the conditionally-instantaneous deformation (observed in a period of time of less than a second).

3. E_2 is the modulus of elasticity. $E_2 = \frac{P}{E_m - E}$, where $E_m - E_0$ is the highly-elastic deformation developing in time.

4. η_1 intrinsic, i. e., the relaxation viscosity of the gel, which characterizes its flow at extremely small rate gradients, not exceeding the rate of thixotropic regeneration of the structure disturbed by shear:
$\eta_1 = \frac{P - P_k}{(d\epsilon/d\tau)_{residual}}$, where $P - P_k$ is the stress acting, maintaining a stationary flow, and $(d\epsilon/d\tau)_{residual}$ is the constant rate of this flow, remaining on completion of the development of the elastic deformation.

5. η_2 is the conventional viscosity of the elastic after-effect characterizing the resistance by increase of the highly-elastic deformation during the first conditionally-small period of deformation $\eta_2 = \frac{P}{(d\epsilon/d\tau)_0 - (d\epsilon/d\tau)_{residual}}$, where $(d\epsilon/d\tau)_0$ is the initial rate of plastic flow.

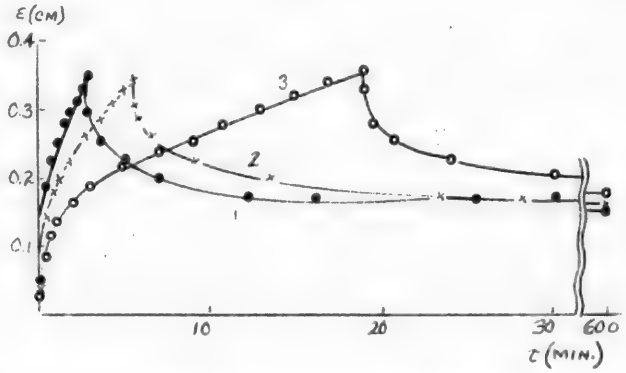


Fig. 2. Kinetics of deformation of 8% ethylcellulose gel. (Sample 348, decalcified).
1) P = 196, 2) P = 143, 3) P = 89 dynes/cm^2.

For determination of all these constants, we used the method of tangential displacement of layers, developed by Veiler and Rebinder [6], with observance of a series of special conditions which we developed earlier (selected spring, range of stress, consideration of elastic deformation of the gel proceeding under the influence of the weight of the layers, etc.) [1].

The data obtained for one of the samples studied is presented in Figs. 2-4. Similar curves were obtained for the other samples. The values of the elasto-plastic properties found on the basis of these graphs for all of the samples studied are cited in Table 1.

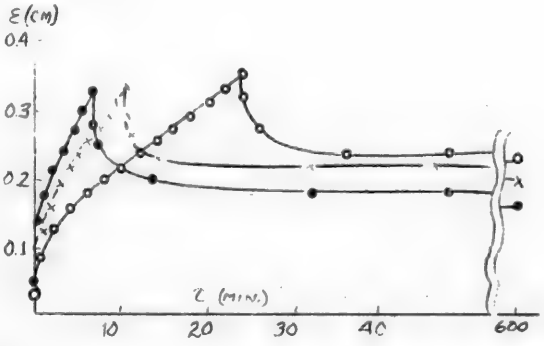


Fig. 3. Kinetics of deformation of 8% ethylcellulose gel. (Sample 348, treated with NaOH).
1) P = 304, 2) P = 250, 3) P = 196 dynes/cm^2.

It is seen from these data that the introduction of small quantities of sodium into the composition of ethyl cellulose considerably increased all the elasto-plastic characteristics of the gel. This relation appeared more graphically for the decalcified Samples 348 and 424. For Sample 224 (non-decalcified) this regularity was somewhat extinguished, since the initial preparation with which we compared the samples treated with NaOH, itself contained a certain quantity of metallic ions, commensurate with the additionally introduced ions (see Table 2). However, in general here also the same regularity appears, i. e., sodium ion considerably increases the elasto-plastic characteristics of the gels. The experiments made with Sample 348, treated with $Ca(OH)_2$, showed that calcium ion increases the elasto-plastic properties of the gels to a greater degree than does sodium ion (Table 3). We see that the stability, hardness and viscosity of the gels are found to be highest in the presence of calcium ions. This is explained certainly by the formation of four-fold bridge bonds of the $-\overset{\overset{O}{\|}}{C}-O-Ca-O-\overset{\overset{O}{\|}}{C}-$, type between the ethylcellulose molecules.

More difficultly explicable is the increase of the elasto-viscous characteristics of the gels under the influence of sodium ions. Relative to the nature of this phenomenon the following assumption may be stated. Between the free carboxyl groups of different molecules of cellulose ester, the formation of hydrogen bonds is possible, which,

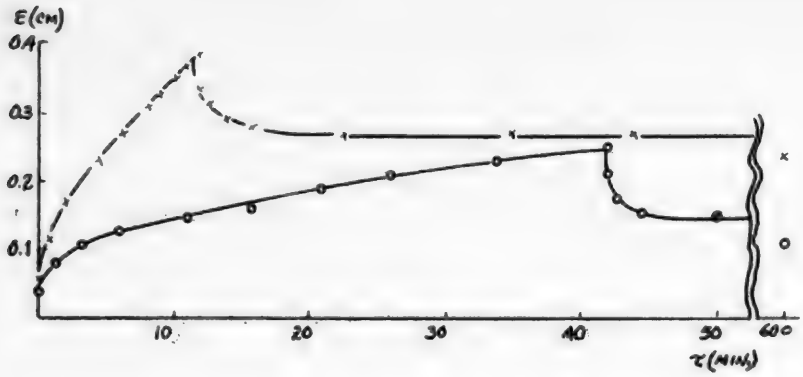


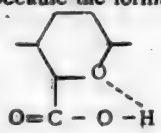
Fig. 4. Kinetics of deformation of 8% ethylcellulose gel. [Sample 348, treated with $Ca(OH)_2$]. 1) P = 2080, 2) P = 1363 dynes/cm^2.

TABLE 3

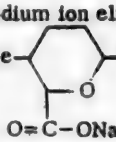
Elasto-plastic Characteristics of Ethylcellulose Gels in Dibutylphthalate

Sample	Concentration of gel (in %)	P_k (in dynes/cm^2)	$E_1 \cdot 10^{-3}$ (in dynes/cm^2)	$E_2 \cdot 10^{-3}$ (in dynes/cm^2)	$\eta_1 \cdot 10^{-5}$ (in poises)	$\eta_2 \cdot 10^{-5}$ (in poises)
224, original	10.0	160	6.0	0.8	4.2	0.2
224, treated with NaOH	10.0	200	18.0	0.9	20.0	0.5
424, decalcified	10.0	240	6.5	1.3	3.3	0.2
424, treated with NaOH	10.0	610	18.0	4.2	5.6	0.8
348, decalcified	8.0	60	3.7	0.4	1.7	0.5
348, treated with NaOH	8.0	100	6.5	1.0	2.4	0.8
348, treated with $Ca(OH)_2$	8.0	1250	31.0	12.5	26.0	–

of course, strengthen the gel structure. But not all the carboxyl groups of the cellulose molecules by far are found to be mutually bound, because the formation of a hydrogen bond is also possible in the cellulose molecule itself, for example, according to the



The replacement of hydrogen in the carboxyl group by sodium ion eliminates such a possibility. In the weakly solvated cellulose ester the solvent or the gel of the sodium type



is not dissociated and between the –COONa dipoles of the adjacent molecules an electrostatic bond arises, the energy of which is somewhat less than that of the hydrogen bond; meanwhile, the number of such bonds appears more significant because, as observed above, the hydrogen bonds can also form inside the cellulose molecule.

SUMMARY

1. It was found that introduction into ethylcellulose of Na^+ ions in the quantity of 0.1% by weight of the ethylcellulose is not reflected by the viscosity of the dilute solutions in mixtures of alcohol with benzene and alcohol with toluene.

2. It was found that all the elasto-plastic characteristics (elastic limit, modulus of elasticity and viscosity) of 8-10% gels of ethylcellulose with dibutylphthalate increased on introduction of 0.1% Na^+ into the ethylcellulose. The Ca^{++} ion increased these characteristics more than did Na^+ ion.

3. A hypothetical explanation for the regularities found for the action of sodium ions on the elasto-plastic characteristics of the gels was given.

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Received July 13, 1953

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INVESTIGATIONS IN THE FIELD OF QUINONES

II. SYNTHESIS OF CHLORO- AND BROMO-SUBSTITUTED HYDROQUINONES BY THE ACTION OF ETHER SOLUTIONS OF HYDROGEN CHLORIDE AND BROMIDE ON QUINONES

A. P. Terentyev, A. N. Grinev and A. B. Terentyev

In 1844 Wöhler [1], studying the properties of p-benzoquinone, found that the latter was converted to chlorohydroquinone by heating with concentrated hydrochloric acid. However, as was found later [2], the production of chlorohydroquinone by this method is associated with a number of complications: part of the substance undergoes resinification, and together with the chlorohydroquinone, hydroquinones containing more than one chlorine atom formed. According to a different method, the reaction between quinone and hydrogen chloride was carried out at room temperature in a solution of chloroform [2, 3] or carbon tetrachloride [4]. This method, used recently for production of a series of chlorohydroquinones (75% yield) is unsatisfactory, because of the length of the reaction and the relatively poor solubility of quinones in chloroform [5]. The chlorination of hydroquinone leads usually to a mixture of 2,3- and 2,5-dichlorohydroquinones [6, 7].

The reaction of p-benzoquinone with concentrated hydrobromic acid or hydrogen bromide in chloroform leads to the formation of a mixture of bromohydroquinone and 2,5-dibromohydroquinone [8, 9]. Thus, until recently a satisfactory method of production of chloro- and bromohydroquinones had not been described fully. It can be assumed that, because of their strong polarization, hydrogen halide molecules will be added more rapidly to the quinone molecule in ether or dioxane solutions, excluding the occurrence of side reactions. As a result of testing this assumption, we developed a method of production of chloro- and bromohydroquinones, according to which the quinone is introduced into reaction with a previously prepared solution of hydrogen chloride or bromide in ether or dioxane. The reaction proceeds quantitatively in 30-40 minutes and requires no strong dilution.

EXPERIMENTAL

1. Production of chlorohydroquinone. 100 g of p-benzoquinone was added in 30-40 minutes by portions at the rate of 5-10 g to ether (200 g) saturated at 0° with hydrogen chloride * (50 g), with cooling and stirring.

The introduction of new portions was carried out only after decolorization of the ether solution. In the flask after distillation of the ether, pure chlorohydroquinone crystallized with a m.p. of 105°, which corresponded to the literature value [2, 3]. The yield was 133 g (quantitative).

If 30 g of p-benzoquinone is added to the ether distillate containing hydrogen chloride, an additional 39.5 g of chlorohydroquinone can be obtained.

2. Production of dichlorohydroquinone. We carried out the reaction just as indicated above, but because of the poorer solubility of dichlorohydroquinone in ether, a larger quantity of ether was used.

100 g of ether, 31 g of hydrogen chloride and 30 g of chloroquinone were used for the experiment. The yield of dichlorohydroquinone (quantitative) was 37.5 g. To the distillate 20 g of quinone was added, and 25 g of dichlorohydroquinone was obtained. The dichlorohydroquinone had a m.p. of 120-128°. 2,6-Dichlorohydroquinone, m.p. 162-163° (m.p. of the quinone 121°), and 2,5-dichlorohydroquinone, m.p. 166-167° (m.p. of quinone 160.5-162°), were obtained by recrystallization from acetic acid and petroleum ether. The melting points corresponded to the literature values [3].

The dichlorohydroquinone with a m.p. of 120-128°, from which we separated 2,5- and 2,6-dichlorohydroquinone, was oxidized to quinone, and by the addition of hydrogen chloride to the latter, trichlorohydroquinone

* An excess of hydrogen chloride of not less than 1/3 of the quantity required by the equation of the reaction was used in the reaction.

with a m.p. of 135°, which corresponded to the literature value [3], was obtained.

3. Production of bromohydroquinone. The reaction was carried out just as in the above-described instances. 50 g of ether, 32 g of hydrogen bromide, and 35 g of p-benzoquinone were used in the experiments. The yield of the bromohydroquinone was 43.5 g (quantitative). Its m.p. was 112-113°, which corresponded to the literature value [9].

The results of all the experiments carried out are recorded in the Table.

Initial quinone	Hydrogen halide	Hydroquinone obtained	Yield	Melting point		Comment
				of substance obtained	literature value	
p-benzoquinone	HCl	chlorohydroquinone	Quantitative	105°	106 [2, 3]	
tolylquinone	HCl	4-chlorotolylhydroquinone	Quantitative	175	175–176 [10]	Isomers separated by recrystallization from petroleum ether
		3-chlorotolylhydroquinone	Quantitative	115–116	115 [11]	
chloro-p-benzoquinone	HCl	2,5-dichlorohydroquinone	Quantitative	166–167	166 [3]	Isomers separated by recrystallization from acetic acid and petroleum ether
		2,6-dichlorohydroquinone	Quantitative	162–163	161 [3]	
dichloroquinone (mixture of isomers)	HCl	trichlorohydroquinone	Quantitative	135	136 [3]	
p-benzoquinone	HBr	bromohydroquinone	Quantitative	112.5	110–111 [9]	
tolylquinone	HBr	4-bromotolylhydroquinone	92%	176	179 [12]	Separated by recrystallization from benzene
bromo-p-benzoquinone	HBr	2,6-dibromohydroquinone	94%	166–167	164 [13]	Separated by recrystallization from benzene
dibromoquinone	HBr	tribromohydroquinone	Quantitative	135	136 [9]	

SUMMARY

A convenient method of production of chloro- and bromohydroquinones by the reaction of quinones with ether solutions of hydrogen chloride and bromide was developed.

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Received March 8, 1954

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THE NITRATION OF 1,1-DIPHENYLETHANE

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The nitro derivatives of diarylethanes recently have attracted attention to themselves as possible insecticides of the DDT type [1] and as raw material for the synthesis of therapeutic preparations [2]. The nitration of chlorinated diarylethanes, $CCl_3CH(AR)_2$, and the reduction forming dinitro compounds, have been studied [3].

The work was begun [4] by nitration of 1,1-diphenylethane in connection with a simple method found for synthesis of the diarylethanes from acetylene and aromatic compounds [5]. Only recently a report has appeared on the nitration of the aromatic nucleus of diphenylethane. Benoit and Eliopoulo [2] obtained small yields of dinitro- and tetranitrodiphenylethanes. A synthesis of mononitrodiphenylethane by means of copper nitrate was proposed in a patent [6].

Konovalov and Yatsevich [7] studied the nitration of the side chain of 1,1-diphenylethane with dilute nitric acid; they demonstrated the formation of diphenylnitroethanol, which is readily converted to diphenylnitroethylene. By these results, the inaccuracy of Anschütz and Römig's earlier works [8] was established, in which the structure of the ester of nitric acid was attributed to the nitration product. Much later, Wieland [9], and also Anscütz [10] confirmed the data of Konovalov and Yatsevich; however, they did not refer to their work. In these new works on the nitration of the side chain of diphenylethane, diphenyldinitroethylene was also described as a product of the action of nitric acid on diphenylethylene.

Thus, the feasibility of production of the following nitro derivatives of 1,1-diphenylethane is contemplated:

$CH_3CH(C_6H_5)(C_6H_4NO_2)$ (I), $CH_3CH(C_6H_4NO_2)_2$ (II), $CH_3CH[C_6H_3(NO_2)_2]_2$ (III),

$(C_6H_5)_2C(OH)CH_2NO_2$ (IV), $(C_6H_5)_2=CHNO_2$ (V), $(C_6H_5)_2C=C(NO_2)_2$ (VI).

We studied the effect of the conditions of nitration on the structure and yields of the products, striving to find preparative methods for the synthesis of the substances enumerated. We were able to improve on previous results [4] of nitration by fuming nitric acid. On slow addition of 1,1-diphenylethane to a four-fold volume of HNO_3 (d 1.5) at −15°, di-(4-nitrophenyl)-ethane (II) was obtained in a yield of 66% of the theoretical. This same product was obtained in a somewhat smaller yield (50%) in nitration experiments with the usual nitrating mixture at 30-50°. The reactions were carried out by introduction of 1 volume of diphenylethane into a mixture of 4 volumes of HNO_3 (d 1.4) and 6 volumes of H_2SO_4 (d 1.84). If these reactions are carried out by heating the mixture at about 100°, a mixture of the dinitro and tetranitro compound (III) is obtained. A considerable yield (45% of the theoretical) of substance (III) was obtained by the use of a large excess of sulfuric acid (2 volumes of HNO_3 and 5 volumes of H_2SO_4).

4,4'-Dinitrobenzophenone and 2,2',4,4'-tetranitrobenzophenone were obtained by oxidation of the nitration products by chromic anhydride; in the same oxidation a certain quantity of 2,4'-dinitrobenzophenone was obtained from the resinous residue from the nitration products. This gave a basis for assuming that, besides the chief p,p-dinitrodiphenylethane, some o,p-isomer also forms. Similar results were obtained by Staedel [11] on nitration of diphenylmethane.

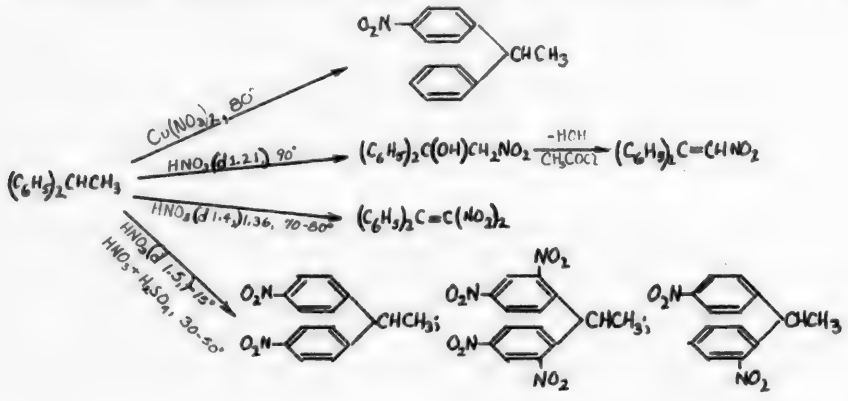
We then proceeded to nitration by means of one volume of nitric acid of different concentrations. In Rinkenbach's work [12] the production of dinitrodibenzyl in a yield of 95% of the theoretical by nitration of dibenzyl with HNO_3 (d 1.42) at 70-80° was described. We repeated this reaction with 1,1-diphenylethane. Instead of product (II), diphenyldinitroethylene (VI) was obtained unexpectedly. The yields of this substance amounted to 80% of the theoretical with somewhat more dilute nitric acid (d 1.365) at 75-80°. On further dilution of the nitric acid, 1,1-diphenyl-1-hydroxy-2-nitroethane (IV) appeared, which became the sole product of the nitration with HNO_3.

(d 1.21) at 80-90° (its yield 53%). Also, in this case, an increase of the reaction temperature to 110° led to accumulation of 1,1-diphenyl-2,2-dinitroethylene (VI).

Thus, we found that the nitration of the side chain of 1,1-diphenylethane proceeds even on heating with concentrated nitric acid. The yields of Substances (IV) and (VI) which we obtained somewhat exceeded those described in the literature [7, 9, 10].

For production of 1-phenyl-1-(4-nitrophenyl)-ethane (I) we used a method described for the nitration of biphenyl [13]. Copper nitrate was added to a solution of 1,1-diphenylethane in acetic anhydride. The mixture was then heated on the water bath. 1-Phenyl-1-(4-nitrophenyl)-ethane (I) was obtained in a yield of 65% of the theoretical.

The results of the nitration of 1,1-diphenylethane under different conditions are presented in the following scheme:



EXPERIMENTAL

1,1-Di-(4-nitrophenyl)-ethane (II). 5 g of 1,1-diphenylethane was introduced dropwise into 20 ml of HNO_3 (d 1.5) with constant shaking. The mixture was cooled to −15°. After addition of all of the diphenylethane, the mixture was poured onto ice at once. The viscous, resinous substance which separated was washed several times with hot and with cold water; after as complete a removal of water as possible, the mixture was triturated with ether. The crystals which separated were filtered off and the resinous residue was again triturated with ether. Such a treatment was repeated until separation of the crystals ceased. 5 g (66%) of 1,1-di-(4-nitrophenyl)-ethane (II) and 3 g of a resinous residue were obtained. After recrystallization from glacial acetic acid Substance (II) consisted of colorless crystals with a m.p. of 112° [4].

4 g (53%) of the same product was obtained by introduction of 5 g of 1,1-diphenylethane into a nitrating mixture of 12.6 ml of HNO_3 (d 1.35) and 19 ml of H_2SO_4 (d 1.84) at 30-35°.

8.03 mg sub.: 0.8232 ml N_2 (33°, 690 mm). 8.52 mg sub.: 0.8869 ml N_2 (33.5°, 688 mm). Found %: N 10.33, 10.46. $C_{14}H_{12}O_4N_2$. Calculated %: N 10.30.

The oxidation of Substance (II) by chromic anhydride gave 4,4'-dinitrobenzophenone with a m.p. of 188°[4].

2,4-Dinitrobenzophenone with a m.p. of 197° was obtained [11] by oxidation of 5 g of the resinous residue with 20 g of chromic anhydride in 120 ml of glacial acetic acid, after a 30-hour boiling of the mixture.

8.98 mg sub.: 0.7938 ml N_2 (20.8°, 718.7 mm). Found %: N 10.41. $C_{13}H_8O_5N_2$. Calculated %: N 10.3.

1,1-Di-(2,4-dinitrophenyl)-ethane (III). 5 g of 1,1-diphenylethane was added gradually at 30-35° to a mixture of 10 ml of HNO_3 (d 1.35) and 25 ml of H_2SO_4 (d 1.84). The light-yellow, resinous substance which formed was washed with soda and with water, and was then triturated with ether. 4.5 g of Substance (III) (45%) and 2 g of a resinous residue were obtained.

After recrystallization from glacial acetic acid, the 1,1-di-(2,4-dinitrophenyl)-ethane (III) consisted of greenish-yellow crystals with a m.p. of 157°.

9.14 mg sub.: 1.2838 ml N_2 (20.4°, 722 mm). 7.37 mg sub.: 1.1172 ml N_2 (20.5°, 715.9 mm). Found %: N 15.55, 15.36. $C_{14}H_{10}O_8N_4$. Calculated %: N 15.46.

2,4,2',4'-Tetranitrobenzophenone with a m.p. of 224° [11] was obtained by oxidation of Substance (III) by chromic anhydride.

1,1-Phenyl-(4-nitrophenyl)-ethane (I). 30 g of copper nitrate was added slowly at 30-35° to a solution of 30 g of 1,1-diphenylethane in 30 ml of acetic anhydride; then the mixture was heated for 5 hours at 85°. The filtered solution was distilled first at ordinary pressure (water, acetic acid and acetic anhydride distilled), then in vacuo. On refractionation, Substance (I) with a b.p. of 180-181° at 7 mm was obtained. The yield was 20 g (65%).

9.22 mg sub.: 0.5488 ml N_2 (22°, 712.1 mm). Found %: N 6.45. $C_{14}H_{13}O_2N$. Calculated %: N 6.12.

2 g of Substance (I) was oxidized by 8 g of CrO_3 in 40 ml of glacial acetic acid by a 7-hour boiling. 1.8 g of 4-nitrobenzophenone with a m.p. of 138° [14] separated.

8.43 mg sub.: 0.4831 ml N_2 (24.8°, 714.3 mm). Found %: N 6.16. $C_{13}H_9O_3N$. Calculated %: N 6.12.

The phenylhydrazone of 4-nitrobenzophenone with a m.p. of 142° [14] was obtained.

1,1-Diphenyl-2,2-dinitroethylene (VI). A mixture of 5 g of 1,1-diphenylethane was heated with 15 ml of HNO_3 (d 1.42) for 6 hours at 70-80° (water bath). A liberation of brown oxides of nitrogen was observed, and the mixture darkened. On pouring it into water, crystals which were impregnated with an oil separated. A total of 4 g (53%) of Substance (VI) and 3 g of oil were obtained.

Substance (VI), recrystallized from acetic acid, consisted of bright-yellow needles with a m.p. of 148°.

8.31 mg sub.: 0.7938 ml N_2 (22°, 715.1 mm). 8.36 mg sub.: 0.8330 ml N_2 (23°, 711.2 mm). Found %: N 10.40, 10.75. $C_{14}H_{10}O_4N_2$. Calculated %: N 10.37.

1,1-Diphenyl-1-hydroxy-2-nitroethane (IV). 5 g of 1,1-diphenylethane was heated with 15 ml of HNO_3 (d 1.21) for 7 hours on the boiling water bath. The treatment was as usual.

3.5 g (50%) of Substance (IV) and 3 g of resinous residue were obtained.

After recrystallization from glacial acetic acid, the 1,1-diphenyl-1-hydroxy-2-nitroethane (IV) consisted of lustrous, snow-white crystals with a m.p. of 108° [7].

From the resinous residue, benzophenone with a m.p. of 46° and an oxime of m.p. 144°, separated.

5.16 mg sub.: 0.2989 ml N_2 (26.6°, 718.2 mm). 5.86 mg sub.: 0.3331 ml N_2 (30.8°, 717.8 mm). Found %: N 6.05, 5.81. $C_{14}H_{13}O_3N$. Calculated %: N 5.76.

Yellow crystals with a m.p. of 88° (V) were obtained by boiling 5 g of Substance (IV) with 10 g of acetyl chloride for 2 hours. The yield was 1.3 g.

8.14 mg sub.: 0.4508 ml N_2 (19°, 718.5 mm). 7.47 mg sub.: 0.4086 ml N_2 (19°, 722 mm). Found %: N 6.12, 6.08. $C_{14}H_{11}O_2N$. Calculated %: N 6.22.

SUMMARY

1. The nitration of 1,1-diphenylethane under different conditions was studied.

2. The feasibility of production of the following substances was shown: di-(4-nitrophenyl)-ethane (66%), di-(2,4-dinitrophenyl)-ethane (53%), phenyl-(4-nitrophenyl)-ethane (65%), diphenyldinitroethylene (80%), diphenylhydroxynitroethane (53%), and diphenylnitroethylene.

3. It was observed that on heating 1,1-diphenylethane with concentrated nitric acid, nitration of the side chain resulted.

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Received February 19, 1954.

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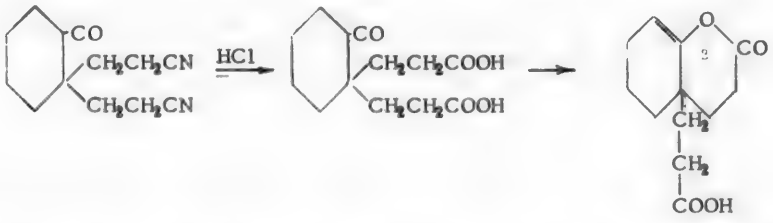
CYANOETHYLATED KETONES IN THE SYNTHESIS OF UNSATURATED δ-LACTONES

II. SYNTHESIS AND PROPERTIES OF THE UNSATURATED δ-LACTONE FROM γ-ACETYLVALERONITRILE

R. Ya. Levina, N. P. Shusherina and M. Yu. Lurye

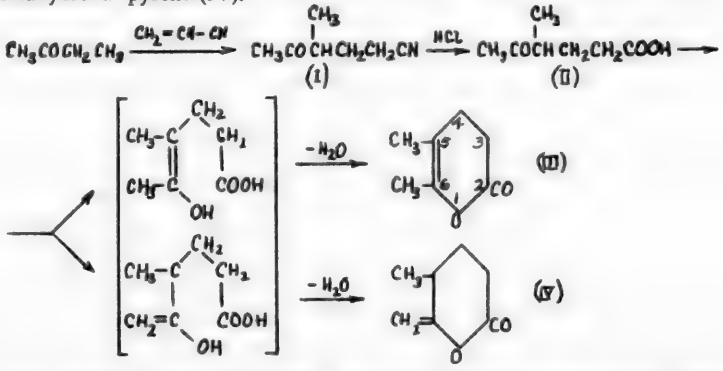
In connection with the presence of unsaturated lactone rings in the molecules of many antibiotics [1], a large number of investigations devoted to the study of the properties of the unsaturated γ-lactones have appeared recently [2]; at the same time, the unsaturated δ-lactones seem to be an almost uninvestigated class of compounds.

Earlier [3] a new method of synthesis of the unsaturated δ-lactones was described, wherein readily available cyanoethylated ketones were used as the starting materials, which were converted to the δ-ketonic acids by hydrolysis, and the unsaturated δ-lactones were formed from the acids by dehydration. The synthesis of the unsaturated δ-lactonic acid from dicyanoethylated cyclohexanone is the chief example of this reaction: *



The presence of the lactonic ring was demonstrated by opening it with an aqueous alkali solution, and also by alcohol in the presence of hydrogen chloride. The unsaturated nature of the resulting lactonic acid was confirmed by the usual reactions for the double bond.

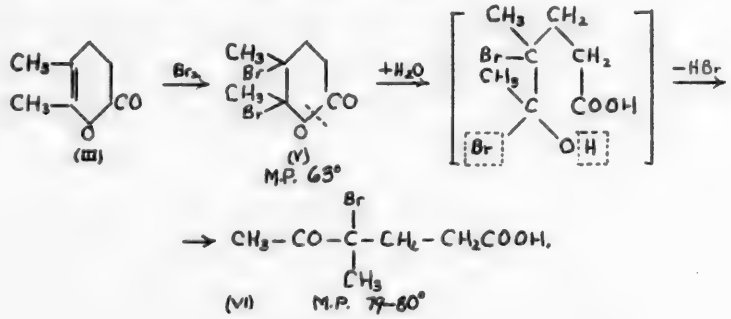
In the present work, the unsaturated δ-lactone from γ-acetylvaleric acid (II), obtained by the hydrolysis of monocyanoethylated methyl ethyl ketone (I), was synthesized by this method (with a yield of 75-85% of the theoretical). On lactonization of γ-acetylvaleric acid, the formation of two unsaturated δ-lactones, differing by the position of the double bond (in the ring and outside of it) is possible – 5,6-dimethyl-3,4-dihydro-α-pyrone (III) and 5-methyl-6-methylene-tetrahydro-α-pyrone (IV):



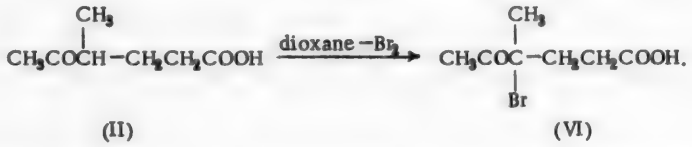
* It is interesting to note that Campbell and coworkers [4], attempting to reduce the ketonic group of a δ-ketonic acid (γ-acetyl-γ-phenylcaproic) by hydriodic acid (KI + H_3PO_4) and red phosphorus, obtained a substance which had a double bond, and which on analysis corresponded to the unsaturated lactone. However, since the substance displayed acid properties, liberating CO_2 from an aqueous soda solution, the authors decided not to ascribe to it the unsaturated δ-lactone structure.

We were able to determine the position of the double bond in the resulting lactone by means of the bromination reaction. The bromination product was the crystalline dibromide (V) with a melting point of 63°, which fumed very violently in the air, and after treatment with water was converted to γ-bromo-γ-acetylvaleric acid (VI) with a melting point of 79-80°.

Such a conversion may be represented by the following scheme:



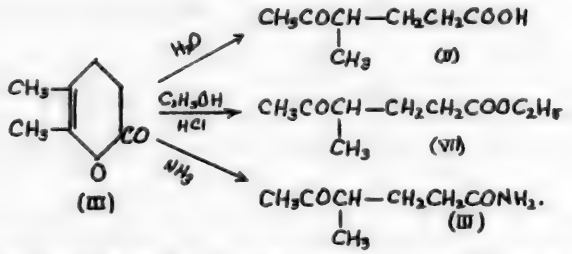
For the identification of the γ-bromo-γ-acetylvaleric acid (VI) which formed, we obtained it by an alternate method – by the bromination of γ-acetylvaleric acid (II) by means of dioxanedibromide. •



The melting point of a sample of a mixture of the γ-bromo-γ-acetylvaleric acid preparations obtained by these two methods showed no depression.

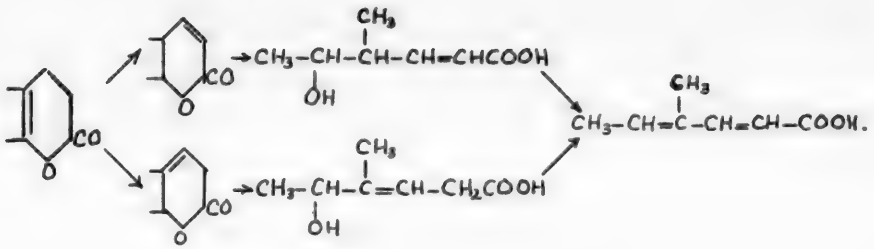
The unusual behavior of the dibromolactone, hydrolyzing unusually easily (under the action of water and even of the moisture of the air) with the splitting off of hydrogen bromide, and its conversion to γ-bromo-γ-acetylvaleric acid, was a definite demonstration that the double bond in the resulting unsaturated lactone is located in the ring, in the vinyl position with respect to oxygen, i.e., that the lactone is 5,6-dimethyl-3,4-dihydro-α-pyrone (III).

The structure of the resulting unsaturated lactone was confirmed also by the ready opening of the lactone ring, with conversion to the original ketonic acid, γ-acetylvaleric (by the action of a dilute aqueous solution of alkali), to its ester (by the action of alcohol and hydrogen chloride), and to its amide (by the action of an aqueous solution of ammonia):



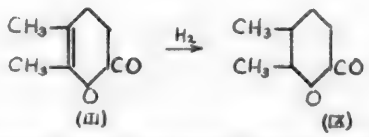
If the double bond in the lactone were not in the vinyl position with respect to the oxygen, but was displaced during the lactonization process toward the CO– group (as occurs on lactonization of the γ-ketonic acids to unsaturated γ-lactones [2]), then as a result of hydrolysis the lactone which we obtained would be converted, not to the original saturated ketonic acid (II), but to the unsaturated hydroxy acid or, after the splitting off of water, to the di-unsaturated acid:

• As is known, the bromination of ketones proceeds with the replacement of the α-hydrogen at the least hydrogenated carbon atom [5].



Thus, it can be considered as demonstrated that no displacement of the double bond toward the CO–group takes place during the process of conversion of the δ-ketonic acid to the unsaturated δ-lactone.

The catalytic hydrogenation of the unsaturated δ-lactone over nickel on aluminum oxide at 200°, led to the production of the saturated lactone, 5,6-dimethyltetrahydro-α-pyrone (IX):



(III) (IX)

The stability of the saturated lactonic ring under catalytic hydrogenation conditions was observed also in the work of Sabatier and Mailhe [6], who obtained the pentanolide-1,4 (α-methylbutyrolactone) by the hydrogenation of levulinic acid over a nickel catalyst at 250°.

EXPERIMENTAL

Monocyanoethylated Methyl Ethyl Ketone (γ-Acetylvaleronitrile)

405 g (5.5 moles) of methyl ethyl ketone and 1 g of a 30% methanol solution of potassium hydroxide were placed in a flask equipped with a stirrer, reflux condenser, dropping funnel and thermometer; on cooling to 3-5° and with vigorous stirring, 30 g (0.54 mole) of acrylonitrile was added at such a rate that the temperature of the reaction mixture did not rise above 10°. Stirring was continued further for about 1 hour; the methyl ethyl ketone which did not react was removed, and the residue was vacuum distilled. 15-20 g (22-30%) of γ-acetylvaleronitrile (I) with a b.p. of 110-112° at 10 mm, and 25 g (50%) of γ-acetyl-γ-methylpimelonitrile with a m.p. of 67° (after recrystallization from benzene), were obtained.

The literature values for γ-acetylvaleronitrile [7]: b.p. 114-115° at 15 mm.

γ-Acetylvaleric acid. A mixture of 30 g of γ-acetylvaleronitrile and 180 ml of dilute (2 : 1) hydrochloric acid was boiled for 3 hours. Then the reaction mixture was diluted with an equal quantity of water and extracted with ether in an extractor for 10 hours. The ether was removed, and the residue was vacuum distilled. The γ-acetylvaleric acid (II), obtained with a quantitative yield, had the following constants:

B. p. 140-141° at 5 mm, n_D^{20} 1.4483, d_4^{20} 1.0674, MR_D 36.12. $C_7H_{12}O_3$. Calc. 36.07.

6.757 mg sub.: 14.072 mg CO_2; 4.980 mg H_2O. 6.430 mg sub.: 13.749 mg CO_2; 4.840 mg H_2O. Found %: C 58.40, 58.34; H 8.48, 8.42. $C_7H_{12}O_3$. Calculated %: C 58.29; H 8.46.

The semicarbazone of γ-acetylvaleric acid melted at 135° (from aqueous alcohol). After three recrystallizations its melting point was unchanged.

5.312 mg sub.: 0.969 ml N_2 (24°, 750 mm). 4.780 mg sub.: 0.878 ml N_2 (22°, 750 mm). Found %: N 20.69, 20.76. $C_8H_{15}O_3N_3$. Calculated %: N 20.89.

According to the literature [7], γ-acetylvaleric acid boils at 160-162° at 16 mm, and its semicarbazone melts at 160-161°.

The ethyl ester of γ-acetylvaleric acid (VII) was obtained (with a 75% yield) by boiling a solution of the acid (10 g) in anhydrous ethyl alcohol (35 ml) in the presence of concentrated sulfuric acid (1 g).

B. p. 95° at 5 mm, n_D^{20} 1.4320, d_4^{20} 0.9803, MR_D 45.51. $C_9H_{16}O_3$. Calc. 45.43.

The semicarbazone had a m.p. of 95-96°. According to the literature [8] the ester had a b.p. of 117-118° at 23 mm.

γ-Bromo-γ-acetylvaleric acid (VI) was obtained with a yield of 90% of the theoretical by the bromination of γ-acetylvaleric acid with dioxanedibromide (by a method developed by Terentyev and Yanovskaya [9] for the bromination of ketones).

M. p. 79-80° (not described in the literature).

5.200 mg sub.: 7.205 mg CO_2; 2.282 mg H_2O. 6.298 mg sub.: 8.675 mg CO_2; 2.828 mg H_2O. Found %: C 37.81, 37.59; H 4.91, 5.02. $C_7H_{11}O_3Br$. Calculated %: C 37.69; H 4.97.

The Unsaturated δ-Lactone from γ-Acetylvaleric Acid (5,6-Dimethyl-3,4-dihydro-α-pyrone; 4-Methylhexenen-4-olide-1,5)

24 g of γ-acetylvaleric acid and 125 ml of acetic anhydride were boiled with several drops of acetyl chloride for 2 hours. The acetic anhydride was removed; the residue was washed several times with small portions of water, dried with magnesium sulfate and vacuum distilled. 18 g (85%) of the unsaturated δ-lactone (III) was obtained, which was a colorless, mobile liquid with a characteristic odor, and which readily decolorized an aqueous solution of permanganate and a solution of bromine in carbon tetrachloride. The lactone had the following constants:

B. p. 210° at 745 mm, 90° at 6-7 mm, n_D^{20} 1.4738, d_4^{20} 1.0552, MR_D 33.62. $C_7H_{10}O_2$. Calc. 33.51.

4.620 mg sub.: 11.290 mg CO_2; 3.390 mg H_2O. 5.987 mg sub.: 14.625 mg CO_2; 4.350 mg H_2O. Found %: C 66.69, 66.66; H 8.12, 8.13. $C_7H_{10}O_2$. Calculated %: C 66.68; H 7.99.

The freshly-distilled lactone displayed no acid properties; on standing, it was partially hydrolyzed by the moisture of the air, being converted to the original ketonic acid.

The resulting unsaturated δ-lactone (5,6-dimethyl-3,4-dihydro-α-pyrone) was not described in the literature.

Bromination of the unsaturated δ-lactone. To a solution of 2 g of the unsaturated lactone in 2 ml of carbon tetrachloride, a solution of 2.5 g of bromine in the same solvent was added, with cooling. The solvent was distilled off in vacuo; the crystalline dibromide (V), after recrystallization from petroleum ether, melted at 63°. The dibromide fumed very violently in the air; after its treatment with water at room temperature a substance with a m.p. of 79-80° (from petroleum ether) was obtained, which contained bromine (Beilstein test) and had acid properties. According to analytical data and according to its melting point, the resulting substance corresponded to γ-bromo-γ-acetylvaleric acid (VI); the melting point of a sample of a mixture with known γ-bromo-γ-acetylvaleric acid (see above) showed no depression. The yield of the bromoketonic acid amounted to 2.8 g (80%).

Hydrolysis of the unsaturated δ-lactone. The lactone (III) was gradually converted to the original γ-acetylvaleric acid by the action of the moisture of the air. Titration by alkali of the lactone which had stood for several days after production showed the presence of appreciable quantities of acid in it. On standing with water for 4 days (at room temperature), the lactone was hydrolyzed by 40-50%. On heating the lactone with a 10% aqueous solution of potassium hydroxide for 1 hour there was a quantitative conversion of it to the ketonic acid, which was identified by its semicarbazone (m.p. 135°).

Ammonolysis of the unsaturated δ-lactone was carried out by shaking it in a funnel with a twofold quantity of concentrated aqueous ammonia. The resulting amide of acetylvaleric acid (not described in the literature) melted at 124° after recrystallization from ethyl acetate.

4.782 mg sub.: 0.424 ml N_2 (20°, 743 mm). 4.666 mg sub.: 0.416 ml N_2 (20°, 743 mm). Found %: N 10.10, 10.16. $C_7H_{13}O_2N$. Calculated %: N 9.77.

Alcoholysis of the unsaturated δ-lactone. A solution of 10 g of the lactone in 75 ml of anhydrous alcohol was saturated with hydrogen chloride, with cooling with ice for 2 hours. The reaction mixture was poured into 150 ml of water and extracted with ether. After the usual treatment, 8 g (66%) of the ester of γ-acetylvaleric acid was separated:

B. p. 95° at 5 mm, n_D^{20} 1.4300; its semicarbazone melted at 96-97°.

A sample of a mixture of the two semicarbazone preparations showed no depression on melting.

A catalytic hydrogenation of the unsaturated δ-lactone (20 g) was carried out over nickel on aluminum oxide at 200°. The catalyzate was washed with soda and with water, dried with calcined magnesium sulfate and

vacuum distilled. The separated hydrogenation product (13 g) did not decolorize bromine water and had no acid properties.

B. p. 107-109° at 8 mm, n_D^{20} 1.4550, d_4^{20} 1.0222, MR_D 34.03. $C_7H_{12}O_2$. Calc. 33.98.

4.100 mg sub.: 9.820 mg CO_2; 3.480 mg H_2O; 4.725 mg sub.: 11.305 mg CO_2; 4.020 mg H_2O. Found %: C 65.36, 65.30; H 9.52, 9.28. $C_7H_{12}O_2$. Calculated %: C 65.59; H 9.42.

SUMMARY

1. A new method of production of unsaturated δ-lactones, with the use of cyanoethylated ketones as the starting materials, was developed.

2. The cyanoethylation of methyl ethyl ketone, hydrolysis of the γ-acetylvaleronitrile which formed to γ-acetylvaleric acid, and lactonization of the latter led to the production (75-85% yield) of the unsaturated δ-lactone, 5,6-dimethyl-3,4-dihydro-α-pyrone (not described in the literature).

3. The structure of the resulting unsaturated δ-lactone (presence of lactone ring) was demonstrated by the opening of the lactone ring, with conversion to the original ketonic acid (hydrolysis) to its ester (alcoholysis) and to the amide (ammonolysis).

4. By bromination of the resulting unsaturated δ-lactone, it was demonstrated that the double bond in it occurred in the ring, in the vinyl position with respect to the oxygen, i.e., that it was 5,6-dimethyl-3,4-dihydro-α-pyrone.

5. By hydrogenation of 5,6-dimethyl-3,4-dihydro-α-pyrone over nickel on aluminum oxide at 200°, the saturated δ-lactone, 5,6-dimethyltetrahydro-α-pyrone (not described in the literature) was obtained.

6. Several new derivatives of γ-acetylvaleric acid were obtained.

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Received February 16, 1954

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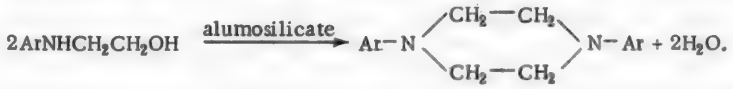
DEHYDRATION OF N-(β-HYDROXYETHYL)-ARYLAMINES IN THE PRESENCE OF ALUMOSILICATE

Yu. K. Yuryev and L. F. Gorin

The dehydration of N-(β-hydroxyethyl)-arylamines, with the formation of the corresponding N,N'-diarylpiperazines, has been studied only in the instances of N-(β-hydroxyethyl)-aniline and N-(β-hydroxyethyl)-p-toluidine. In the case of N-(β-hydroxyethyl)-p-toluidine the closing of the piperazine ring took place readily with ordinary boiling [1], whereas N-(β-hydroxyethyl)-aniline was not changed by heating with anhydrous oxalic acid [2], and N,N'-diphenylpiperazine was formed only by the action of phosphorus pentoxide in boiling xylol [3] or by heating with a copper-chromium catalyst at 250° under a hydrogen pressure of 250 atm [4].

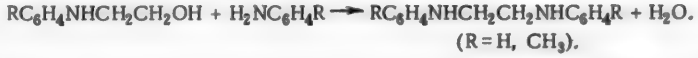
Later one of us [5] showed that N,N'-diphenylpiperazine was formed readily by heating N-(β-hydroxyethyl)-aniline with alumo-silicate at 240°.*

In the present work we carried out the dehydration of different N-(β-hydroxyethyl)-arylamines under the action of alumosilicate, and obtained the corresponding symmetrical N,N'-diarylpiperazines



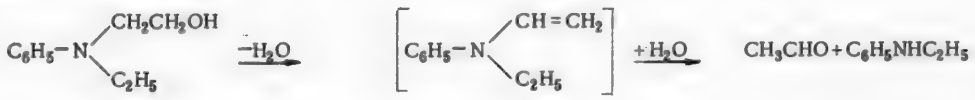
$$2\,ArNHCH_2CH_2OH \xrightarrow{\text{alumosilicate}} Ar-N\begin{matrix}CH_2-CH_2\\ \\ CH_2-CH_2\end{matrix}N-Ar + 2H_2O.$$

By the joint dehydration of N-(β-hydroxyethyl)-aniline, and also of N-(β-hydroxyethyl)-p-toluidine with aniline and with p-toluidine in the presence of alumosilicate, we obtained N,N'-diphenylethylenediamine and N-phenyl-N'-p-tolylethylenediamine, respectively

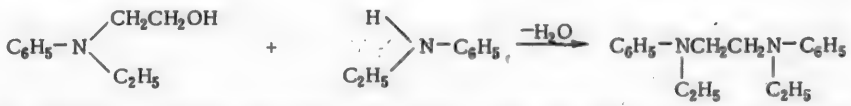


$$RC_6H_4NHCH_2CH_2OH + H_2NC_6H_4R \rightarrow RC_6H_4NHCH_2CH_2NHC_6H_4R + H_2O.$$
$$(R = H,\ CH_3).$$

The heating of N-(β-hydroxyethyl)-N-ethylaniline with alumosilicate at 250-260° led to the production of N,N'-diethyl-N,N'-diphenylethylenediamine, apparently, via the stage of formation of N-vinyl-N-ethylaniline, the hydrolysis of the latter [6], and the joint dehydration of the original N-(β-hydroxyethyl)-N-ethylaniline with the N-ethylaniline which formed

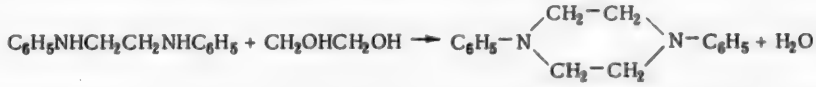


$$C_6H_5-N\begin{matrix}CH_2CH_2OH\\ \\ C_2H_5\end{matrix} \xrightarrow{-H_2O} \left[C_6H_5-N\begin{matrix}CH=CH_2\\ \\ C_2H_5\end{matrix}\right] \xrightarrow{+H_2O} CH_3CHO + C_6H_5NHC_2H_5$$



$$C_6H_5-N\begin{matrix}CH_2CH_2OH\\ \\ C_2H_5\end{matrix} + \begin{matrix}H\\ \\ C_2H_5\end{matrix}N-C_6H_5 \xrightarrow{-H_2O} C_6H_5-N(C_2H_5)-CH_2CH_2-N(C_2H_5)-C_6H_5$$

Finally, N,N'-diphenylpiperazine was obtained by means of the joint dehydration of N,N'-diphenylethylenediamine with ethylene glycol under the same conditions



$$C_6H_5NHCH_2CH_2NHC_6H_5 + CH_2OHCH_2OH \rightarrow C_6H_5-N\begin{matrix}CH_2-CH_2\\ \\ CH_2-CH_2\end{matrix}N-C_6H_5 + H_2O$$

The diarylpiperazines and diarylethylenediamines, obtained in the present work, are cited in the Table.

* We obtained N,N'-diphenylpiperazine with a yield of 54%.

Initial Substance	Reaction products	Melting point	Yield (in % of the theoretical)
N-(β-hydroxyethyl)-aniline	N,N'-diphenylpiperazine	163°	54
N,N'-diphenylethylenediamine + ethylene glycol	N,N'-diphenylpiperazine	163	90
N-(β-hydroxyethyl)-p-toluidine	N,N'-di-p-tolylpiperazine	189	95
N-(β-hydroxyethyl)-o-toluidine	N,N'-di-o-tolylpiperazine	174	27
N-(β-hydroxyethyl)-p-anisidine	N,N'-di-p-anisidylpiperazine	233	50
N-(β-hydroxyethyl)-o-anisidine	N,N'-di-o-anisidylpiperazine	139	10
N-(β-hydroxyethyl)-o-chloroaniline	N,N'-di-o-chlorophenylpiperazine	180	16.5
N-(β-hydroxyethyl)-α-naphthylamine	N,N'-di-α-naphthylpiperazine	265	15
N-(β-hydroxyethyl)-aniline + aniline	N,N'-diphenylethylenediamine	65	40
N-(β-hydroxyethyl)-aniline + p-toluidine	N-phenyl-N'-p-tolylethylenediamine	59	80
N-(β-hydroxyethyl)-p-toluidine + aniline	N-phenyl-N'-p-tolylethylenediamine	59	67.5
N-(β-hydroxyethyl)-N-ethylaniline	N,N'-diethyl-N,N'-diphenylethylenediamine	71	63

It is evident from the data of the Table that the presence of methyl or methoxyl in the para-position – both in N-(β-hydroxyethyl)-arylamine, and in arylamine – conditions the production of a higher yield of N,N'-diarylpiperazine and, consequently, of N,N'-diarylethylenediamine. The yields of the reaction products decreased sharply with the presence of these groups in the ortho-position.

EXPERIMENTAL

Production of N,N'-Diarylpiperazines from N-(β-Hydroxyethyl)-arylamines

1. N,N'-Di-p-tolylpiperazine. 15.0 g of N-(β-hydroxyethyl)-p-toluidine and 3 g of alumosilicate cracking catalyst were heated for 5 hours in a small retort at 230–240° in a nitrogen atmosphere. 1.8 g of water was distilled off. After cooling, the reaction substance was completely crystallized. The crude reaction product melted at 177°; after washing with ether and after recrystallization from alcohol the substance melted at 189° and consisted of N,N'-di-p-tolypiperazine. The yield was 12.6 g (95%).

Found %: N 10.46, 10.50. $C_{18}H_{22}N_2$. Calculated %: N 10.52.
Literature data for N,N'-di-p-tolylpiperazine: Demole [1], m.p. 189–190°, Bischoff [7], m.p. 187°.

2. N,N'-Di-o-tolylpiperazine. On heating 30.2 g of N-(β-hydroxyethyl)-o-toluidine with 6 g of alumosilicate, 3.2 g of water was distilled off. The crystals which separated on cooling the reaction substance, after washing with ether and after recrystallization from alcohol, melted at 174° and consisted of N,N'-di-o-tolylpiperazine. The yield was 7.5 g (27%).

Found %: N 10.42, 10.70. $C_{18}H_{22}N_2$. Calculated %: N 10.52.
Literature value for N,N'-di-o-tolypiperazine: Bischoff [7], m.p. 174°.

3. N,N'-Di-p-anisidylpiperazine. On heating 20 g of N-(β-hydroxyethyl)-p-anisidine with 4 g of alumosilicate, 0.4 g of water was distilled. After vacuum distillation of the unchanged N-(β-hydroxyethyl)-p-anisidine (13.5 g), the residue crystallized. After washing with a mixture of chloroform and alcohol and recrystallization from pyridine, the crystals melted at 233° and consisted of N,N'-di-p-anisidylpiperazine. The yield was 3 g [50% on the basis of the N-(β-hydroxyethyl)-p-anisidine used in the reaction].

Found %: N 9.66, 9.62. $C_{18}H_{22}O_2N_2$. Calculated %: N 9.39.
Literature value for N,N'-di-p-anisidylpiperazine: Bischoff [7], m.p. 233°.

4. N,N'-Di-o-anisidylpiperazine. On heating 20 g of N-(β-hydroxyethyl)-o-anisidine with 4 g of alumosilicate, 0.2 g of water was distilled. The crystals which separated on cooling, were filtered and washed with a mixture of chloroform and alcohol. After recrystallization from pyridine they melted at 139° and consisted of N,N'-di-o-anisidylpiperazine. The yield was 1.8 g (10%).

Found %: N 9.65, 9.42 $C_{18}H_{22}O_2N_2$. Calculated %: N 9.39.

N,N'-Di-o-anisidylpiperazine was difficulty soluble in alcohol, chloroform and benzene, and more readily soluble in ether; it was not described in the literature.

5. N,N'-Di-o-chlorophenylpiperazine. From 10 g of N-(β-hydroxyethyl)-o-chloroaniline, heated with 2 g of alumosilicate, as described above, N,N'-di-o-chlorophenylpiperazine was obtained, which after washing with ether and after recrystallization from anhydrous alcohol melted at 180°. The yield was 1.5 g (16.5%). The N,N'-Di-o--chlorophenylpiperazine was highly soluble in chloroform, and less soluble in ether and in alcohol; it was not described in the literature.

Found %: N 9.52, 9.46. $C_{16}H_{16}N_2Cl_2$. Calculated %: N 9.82.

6. N,N'-Di-α-naphthylpiperazine. 10.2 g of N-(β-hydroxyethyl)-α-naphthylamine was heated with 2 g of alumosilicate. The unreacted N-(β-hydroxyethyl)-α-naphthylamine (6 g) was vacuum distilled. On addition of alcohol to the residue N,N'-di-α-naphthylpiperazine crystallized out, which was filtered off, washed with a mixture of ether and alcohol, and after recrystallization from pyridine, melted at 265°. The yield was 0.6 g [15% of the theoretical, on the basis of the N-(β-hydroxyethyl)-α-naphthylamine used].

Found %: N 8.47, 8.47. $C_{24}H_{22}N_2$. Calculated %: N 8.28.
Literature value for N,N'-di-α-naphthylpiperazine: Bischoff [7], m.p. 265°.

Production of N,N'-Diarylethylenediamines

1. N,N'-Diphenylethylenediamine. 13.7 g (0.1 mole) of N-(β-hydroxyethyl)-aniline and 58.5 g (0.6 mole) of aniline were heated for 5 hours at 230-240° with 14.5 g of alumosilicate in a flask with a fractionating column and a reflux condenser. 18 g of a mixture of aniline and water was distilled. After removal of the alumosilicate by filtration, 42 g of aniline and 0.5 g of N-(β-hydroxyethyl)-aniline were driven off by vacuum distillation. From the residue, by the addition of 80% alcohol, 2.5 g (21.7%) of N,N'-diphenylpiperazine with a m.p. of 153° was crystallized, which after recrystallization from 80% alcohol melted at 163°; a sample of a mixture with known N,N'-diphenylpiperazine disclosed no depression.

N,N'-Diphenylethylenediamine, melting at 65° after repeated recrystallization from alcohol, separated from the filtrate on dilution with water. The yield was 8.5 g (40%). A sample of a mixture with known N,N'-diphenylethylenediamine disclosed no depression.

Found %: N 13.03, 13.19. $C_{14}H_{16}N_2$. Calculated %: N 13.08.
Literature data for N,N'-diphenylethylenediamine: Bischoff [8], m.p. 65°.

2. N-Phenyl-N'-p-tolylethylenediamine. a) 13.7 g (0.1 mole) of N-(β-hydroxyethyl)-aniline and 64 g (0.6 mole) of p-toluidine were heated for 5 hours with 15 g of alumosilicate at 230-240°, as described above. 14 g of a mixture of p-toluidine and water was distilled off. After removal of the alumosilicate by filtration, the following fractions were separated by vacuum distillation of the reaction product at 4 mm: 1st, b.p. 55°, 40 g, with a m.p. of 45° (p-toluidine); 2nd, b.p. 55-138°, 1.2 g; 3rd, b.p. 138-139°, 1.1 g, n_D^{20} 1.5763 and d_4^{20} 1.0941 [N-(β-hydroxyethyl)-aniline]; 4th, b.p. 139-198°, 2.2 g; 5th, b.p. 198-200°, 18.3 g. The 5th fraction was crude N-phenyl-N'-p--tolylethylenediamine (m.p. 55°), the purification of which was attained by fractional precipitation with water from alcoholic solution; the impurities came down first, but on further dilution crystals of pure N-phenyl-N'-p-tolylethyenediamine with a m.p. of 58-59° separated, which were leaflets with a mother-of-pearl luster, readily soluble in alcohol and in ether, and very difficulty soluble in water. The yield was 18 g (80%).

Found %: N 12.40, 12.38. $C_{15}H_{18}N_2$. Calculated %: N 12.27.

b) 15.1 g (0.1 mole) of N-(β-hydroxyethyl)-p-toluidine and 55 g (0.6 mole) of aniline were heated with 17 g of alumosilicate for 5 hours at 230-240° as described above. 24 g of aniline and water were distilled off. After removal of the alumosilicate by filtration, the following fractions were separated by vacuum distillation of the reaction product at 5 mm: 1st, b.p. 52-53°, 24 g, n_D^{20} 1.5841 and d_4^{20} 1.0223 (aniline); 2nd b.p. 53-146°, 1.2 g, n_D^{20} 1.5793; 3rd, b.p. 146-147°, 2.4 g with a m.p. of 42° [N-(β-hydroxyethyl)-p-toluidine]; 4th b.p. 147-199°, 1.5 g; 5th, b.p. 199-213°, m.p. 54°, 15.3 g – N-phenyl,N'-p-tolylethylenediamine.

By fractional precipitation of the alcoholic solution of the 5th fraction with water (as described above), 13 g 67.5% of N-phenyl, N'-p-tolylethylenediamine was separated, which after drying in vacuo and after recrystallization from alcohol melted at 59° and was identical with the N-phenyl-N'-p-tolylethylenediamine obtained in the

previous experiment; a sample of a mixture disclosed no depression (m.p. 59°).

3. N,N'-Diethyl-N,N'-diphenylethylenediamine. 24 g (0.14 mole) of N-(β-hydroxyethyl)-N-ethylaniline and 5 g of alumosilicate were heated for 4 hours at 250-260°. The reaction product was fractionated in vacuo, whereby the following fractions were separated: 1st b.p. up to 190° (15 mm), 3 g; 2nd, b.p. 190-200° (2 mm), 16 g; residue, 3 g.

12 g (63%) of a substance going over at 194-196° (2 mm) and crystallizing on standing was obtained by redistillation of the 2nd fraction. The substance melted at 71° after recrystallization from alcohol and consisted of N,N'-diethyl-N,N'-diphenylethylenediamine.

Found %: N 10.56, 10.52. $C_{18}H_{24}N_2$. Calculated %: N 10.44.
Literature value for N,N'-diethyl-N,N'-diphenylethylenediamine: Hoffmann [9] - m.p. 70°, Frohlich [10], m.p. 75°.

Production of N,N'-Diphenylpiperazine from N,N'-Diphenylethylenediamine and Ethylene Glycol

3 g of N,N'-diphenylethylenediamine and 0.6 g of ethylene glycol were heated with 0.7 g of alumosilicate, as described in experiment 1, 2 (b), for 6 hours at 230-240°. 2.9 g (90%) of N,N'-diphenylpiperazine with a m.p. of 163° was obtained after removal of the catalyst, washing with water and with ether, and after recrystallization from alcohol. A sample of a mixture with known N,N'-diphenylpiperazine disclosed no depression.

The picrate (from alcohol) consisted of yellow needles with a m.p. of 172-173°. A sample of a mixture with the known picrate of N,N'-diphenylpiperazine disclosed no depression.

Literature values for N,N'-diphenylpiperazine: Yuryev and Novitsky [5] – m.p. 163°, picrate m.p. 172-173°; Korshak and Strepikheev [11] – m.p. 163-164°, Pollard [4] – m.p. 163.5-164.5°; C. Bischoff [7] – m.p. 163°.

SUMMARY

1. The dehydration of N-(β-hydroxyethyl)-arylamines in the presence of alumosilicate at 230-240° led to the production of symmetrical N,N'-diarylpiperazines.

2. The joint dehydration of N-(β-hydroxyethyl)-arylamines with aromatic amines in the presence of alumosilicate led to N,N'-diarylethylenediamines and may serve as a method of production of both symmetrical and asymmetrical N,N'-diarylethylenediamines.

3. The heating of N-(β-hydroxyethyl)-N-ethylaniline with alumosilicate at 250-260° led to N,N'-diethyl-N,N'-diphenylethylenediamine.

4. The joint dehydration of N,N'-diphenylethylenediamine with ethylene glycol in the presence of alumosilicate led to the production of N,N'-diphenylpiperazine and may serve as a method of production of asymmetrical N,N'-diarylpiperazines.

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Received March 4, 1954

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PRODUCTION OF β-n-AMYL- AND β-PHENYLTHIOPHANE BY CATALYTIC CONVERSION OF THE CORRESPONDING FURANIDINES

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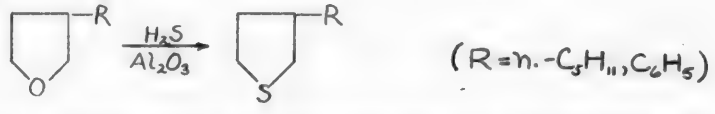
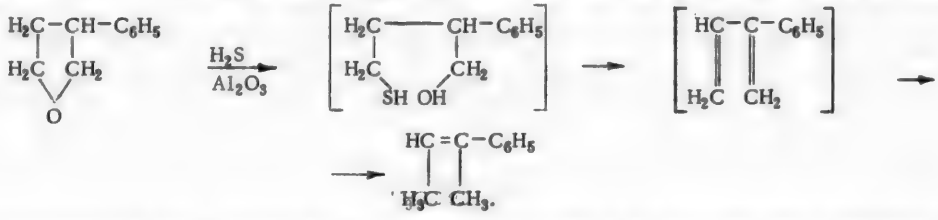
In the catalytic conversion of oxygen-containing heterocycles to cycles with other hetero-atoms, described and studied by one of us, both α-alkyl- [1] and β-alkylfuranidines [2], and also dialkylfuranidines of different structure [3], were included. By the action of hydrogen sulfide on them in the presence of aluminum oxide at an elevated temperature they all were converted with high yields to their corresponding thiophanes. β-Methyl-, β-ethyl-, β-propyl-, and β-butylthiophanes were obtained by such a method from the β-alkylfuranidines with yields of 72-81% [2], by which it was found that an increase of the number of carbon atoms in the side chain of the β-alkylfuranidines is related to the yield of the thiophane homologs to a lesser degree than in the conversion of the α-alkylfuranidines.

In the present work the effect on the conversion process of further complication of the alkyl in the initial β-alkylfuranidine, and also the effect on the conversion process of the phenyl radical in β-phenylfuranidine, were studied. β-Amylthiophane, with a yield of 64%, was obtained by passing β-n-amylfuranidine over aluminum oxide in a current of hydrogen sulfide. Under the same conditions β-phenylfuranidine gave β-phenylthiophane with a yield of 58%.



A by-product of the transformation of β-phenylfuranidine was 2-phenylbutene-2, the formation of which may be represented as a result of the opening of the oxide ring under the action of hydrogen sulfide, with the formation of 1-hydroxy-2-phenylbutane-4-thiol, followed by the splitting off of water and hydrogen sulfide from it, with the formation of 2-phenylbutadiene, and reduction of the latter with the addition of hydrogen in the 1,4-position.



In previous works on the conversion of α- and β-alkylfuranidines to the corresponding thiophanes no formation of reaction by-products was observed; therefore, it is certain that the possibility of the partial splitting off of water and hydrogen sulfide from the di-primary intermediate 1,4-mercapto compound was conditioned by the effect of the phenyl radical located on the β-carbon atom of the furanidine ring.

One of us observed the simultaneous splitting off of water and hydrogen sulfide with the formation of unsaturated hydrocarbons only for those γ-oxides which, by the action of hydrogen sulfide, probably in the intermediate stage, give a di-tertiary or, but to a lesser degree, primary-tertiary, 1,4-mercaptohydroxy compound, as occurred, for example, in the instance of the introduction of 2,2,5,5-tetramethylfuranidine [4] or, correspondingly, 2,2-dimethylfuranidine, into the reaction [5].

Thus, the secondary formation of 2-phenylbutene-2 serves as an additional confirmation of the validity of the proposal by one of us of a scheme for the mechanism of the catalytic conversion of oxygen-containing heterocycles to cycles with other hetero-atoms [6].

As to a further increase of the number of carbon atoms in the side chain of the β-alkylfuranidines, it should be noted that this again conditions a certain decrease of the corresponding thiophane homolog yield; according to the reaction described, β-n-butylthiophane was obtained with a yield of 79% [2], whereas in the present work β-n-amylthiophane was obtained with a yield of 64%.

EXPERIMENTAL

β-n-Amylfuranidine and β-phenylfuranidine were passed at a rate of 5-6 drops per minute into a strong current of hydrogen sulfide through a tube with an internal diameter of 10 mm, which was filled with aluminum oxide (length of catalyst layer 40 cm) and heated at about 350°. The receiving vessel was cooled with snow and salt. The catalyzate was extracted with ether. The ether extracts of the catalyzates were washed with an alkali solution and dried with fused potassium hydroxide. After driving off the ether the reaction product was vacuum distilled.

β-n-Amylthiophane. 4.25 g (64%) of β-n-amylthiophane was obtained from 6 g of β-n-amylfuranidine (b.p. 69-70° at 12 mm, n_D^{20} 1.4378, d_4^{20} 0.8602 [7]). This was a colorless liquid with a characteristic odor, soluble in ether, alcohol, and acetone, and having the following constants:

B.p. 92–93° (10 mm), n_D^{20} 1.4870, d_4^{20} 0.9151, MR_D 49.75. $C_9H_{18}S$. calc. 49.63.
Compound with $HgCl_2$ m.p. 89.5–90.5° (from alcohol). Found %: S 20.24, 20.35.
$C_9H_{18}S$. Calculated %: S 20.25.

β-n-Amylthiophane was not described in the literature.

β-Phenylthiophane. 4.3 g (58%) of β-phenylthiophane, having the following constants, was obtained from 6.7 g of β-phenylfuranidine (b.p. 81.5-82.5° at 4 mm, n_D^{20} 1.5442, d_4^{20} 1.0448) [7]:

B.p. 112–113° (5 mm), m.p. 6°, n_D^{20} 1.6000, d_4^{20} 1.1009, MR_D 51.10. $C_{10}H_{12}SF_3$. calc. 50.65.
Compound with $HgCl_2$: m.p. 187–187.5° (from alcohol).
Found %: S 19.41, 19.38. $C_{10}H_{12}S$. Calculated %: S 19.51

β-Phenylthiophane was not described in the literature.

1.2 g of a considerably lower-boiling fraction, which decolorized bromine water and after redistillation had the following constants, was also separated on distillation of the reaction product:

B.p. 181–183° (742 mm), n_D^{20} 1.5300, d_4^{20} 0.9034, MR_D 44.28. $C_{10}H_{12}F_4$. calc. 44.31.
Found %: C 91.06, 90.89; H 9.02, 9.08. $C_{10}H_{12}$. Calculated %: C 90.90; H 9.09.

According to its analytical data, constants and properties, the substance obtained was 2-phenylbutene-2.

Literature values for 2-phenylbutene-2: B.p. 186–187° [8]; b.p. 188–191° (760 mm), d_4^{22} 0.909, n_D^{22} 1.5288 [9]; b.p. 80–81° (20 mm), d_4^{25} 0.8911, n_D^{25} 1.5299 [10]; b.p. 184–187° (752.9 mm), d_4^{20} 0.9041, n_D^{21} 1.5299 [11].

The presence of one double bond was established by bromination with a solution of bromine in chloroform at −12°.

0.1902 g sub.: consumed for titration 0.224 g bromine; theoretically required quantity of bromine: 0.230 g.

Benzoic acid with a m.p. of 121° was obtained by oxidation with potassium permanganate in a neutral solution. A sample of a mixture with known benzoic acid displayed no melting point depression.

SUMMARY

1. β-n-Amylfuranidine and β-phenylfuranidine were converted to β-n-amylthiophane and β-phenylthiophane, respectively, under the conditions of catalytic conversion of oxygen-containing hetero-cycles to cycles with other hetero-atoms.

2. On conversion of β-phenylfuranidine to β-phenylthiophane, the formation of a by-product of the reaction, 2-phenylbutene-2, took place, which was conditioned by the effect of the phenyl radical bound to the β-carbon atom of the furanidine ring.

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Received March 22, 1954

Moscow State University

* T.p. = C. B. Translation pagination.

THE MECHANISM OF HETEROGENEOUS CATALYTIC ISOMERIZATION OF HYDROCARBONS BY ACID CATALYSTS

II. MECHANISM OF FORMATION OF TERPINOLENE AND TERPINENES BY CATALYTIC ISOMERIZATION OF PINENE AND LIMONENE BY TITANIC ACID

G. A. Rudakov, M. M. Shestaeva, A. T. Marchevsky and Z. S. Khomenko

It was shown in a previous report [1] that limonene and camphene are rapidly isomerized and racemized by heating with titanic acid, and that at the same time, these terpenes, soluble in pinene, do not undergo changes on heating with the same catalyst in the presence of a sufficient concentration of pinene in solution.

This earlier, unknown characteristic of the isomerization transformations of terpenes enabled us to carry out a further investigation, interpreting the mechanism of isomerization of pinene to terpinolene, and also of pinene and limonene to α- and γ-terpinenes, on heating with titanic acid.

Besides camphene and limonene (II), terpinolene (III) is formed by the catalytic isomerization of pinene (I) on clays, titanic acid and other catalysts. Since, in its turn, limonene is readily isomerized to terpinolene, it was impossible until recently to answer with complete definiteness the question of whether terpinolene, obtained by the catalytic isomerization of pinene, was a product of the isomerization of both pinene and limonene, or was the product of the isomerization of only the latter. Considering the reaction from the point of view of ideas already stated [1, 2], it can be assumed that terpinolene should be obtained not only as a result of the isomerization of limonene, but also directly from pinene, since the conversion of pinene to limonene and to terpinolene must be brought about via the formation of the same intermediate compound or the ion (IV) corresponding to it.

We were able to solve the problem experimentally after it became known that the conversion of linonene to terpinolene by titanic acid did not take place in the presence of pinene, if the content of the latter in a solution of the isomerization products was above 25-30%. For this it was necessary to investigate the composition of the products of the incomplete isomerization of pinene, by stopping at the pinene content in the isomerizate, by eliminating the formation of terpinolene from limonene. The investigation showed the presence of terpinolene in the isomerizates containing unreacted pinene and, consequently, undoubtedly its primary origin. Since terpinolene and limonene formed from the same intermediate compound, the ratio between them remained constant until a sufficient quantity of pinene was present in the solution to render impossible the secondary reaction of the conversion of limonene to terpinolene. Only after the content of the unreacted pinene fell below a definite limit did the increase of the terpinolene content in the reaction products begin (see Table).

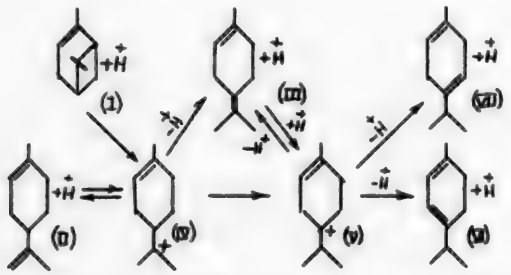
The resulting ratio between the quantities of limonene and terpinolene which formed during the initial period of the reaction, i.e., in the presence of above 25-30% of pinene in solution, enabled us to determine the approximate ratio of the rates of conversion of pinene to limonene and to terpinolene as 3:1.

As to the α- and β-terpinenes obtained by the acid isomerization of pinene and limonene, they are usually considered as secondary reaction products. It is assumed the terpinenes are formed from terpinolene, which is obtained from pinene and limonene at an early stage of the reaction. Such a view is probably based on the assumption that the reaction in the present case consists of a series of consecutive additions of acid to the double bond of the hydrocarbon and is the reverse of cleavages.

Considering the reaction as ionic, the terpinenes forming from pinene and limonene may be considered as not only secondary, but also as primary reaction products.

Composition of the Monocyclic Terpenes Obtained from Pinene by Catalytic Isomerization by Titanic Acid, in Relation to the Extent of Conversion

Experiment	Temperature of experiment	Charge of catalyst (in %)	Per cent of unreacted pinene	Composition of monocyclic terpenes (in %)		
				limonene	terpinolene	α-terpinene
1	135°	0.5	76	68	27	2.9
2	160	0.07	72	67	26	3.2
3	160	0.2	46	72	23	3.2
4	160	0.1	32	62	31	3.3
5	160	0.2	0	50	40	7.5



Gaining a proton from the catalyst, pinene and limonene are converted to the carbonium ion (IV). If titanic acid or a pinene-insoluble catalyst analogous to it is used as the catalyst, carbonium ion will exist only on the surface of the catalyst in the composition of a compound of the $\overset{+}{R}\overline{X}$ [1] type, which does not prevent its undergoing all the rearrangements characteristic of carbonium ions [3-5]. The isomerization of part of the ions (IV) to ions (V) is most likely in the present case. The (V) ions, returning the proton to the catalyst, should be converted to terpinenes (VI) and (VII) or to terpinolene (III).

If the presence of a direct conversion of pinene or limonene to terpinenes without the formation of terpinolene as the necessary intermediate product should be demonstrated, then a serious basis for the use of the ionic mechanism of this reaction would be obtained.

After it became known that the isomerization conversion of limonene by titanic acid did not occur if α-pinene was present in sufficient concentration in the solution of terpenes reacting, there was assurance that terpinolene also close in structure to limonene, likewise would not isomerize in the presence of pinene. It was therefore possible, to a high degree of probability, to solve the problem of the presence of a direct conversion of pinene (and consequently, also limonene) to terpinenes by the presence of α- and γ-terpinenes, or even relatively easily by determining the α-terpinene in the monocyclic terpenes obtained by the incomplete isomerization of pinene. An investigation of these monocyclic terpenes not only established the presence of α-terpinene in them, but also showed that the ratio between the limonene, terpinolene and α-terpinene contained in the monocyclic terpenes was maintained constant until there was a sufficient quantity of pinene in the solution, and only with a decrease of the pinene concentration below 30% did the terpinolene and α-terpinene contents in the monocyclic terpenes begin to increase, and the limonene content to decrease (see Table). Such a course of the process definitely confirmed the primary origin of the α-terpinene at the initial stage of the reaction, which terminated at a sufficiently high pinene concentration in the solution. If at this stage of the reaction α-terpinene is not obtained directly from pinene, but from terpinolene, the α-terpinene content in the monocyclic terpenes would not be maintained constant, but would increase continuously, since the rate of formation of the terpinenes would increase with an increase of the terpinolene concentration in the solution. The increase of the α-terpinene content in the monocyclic terpenes after decrease of the pinene content in the solution below 30% indicates the beginning of the formation of α-terpinene from terpinolene.

The statement confirms the above-developed ionic scheme of the formation of terpinenes from pinene and limonene.

EXPERIMENTAL

Starting materials. The α-pinene used for the investigation was isolated from Pinus sylvestris turpentine. The physical properties of the α-pinene were: d_4^{20} 0.8582, n_D^{20} 1.4655, $[\alpha]_D$ + 29.6°.

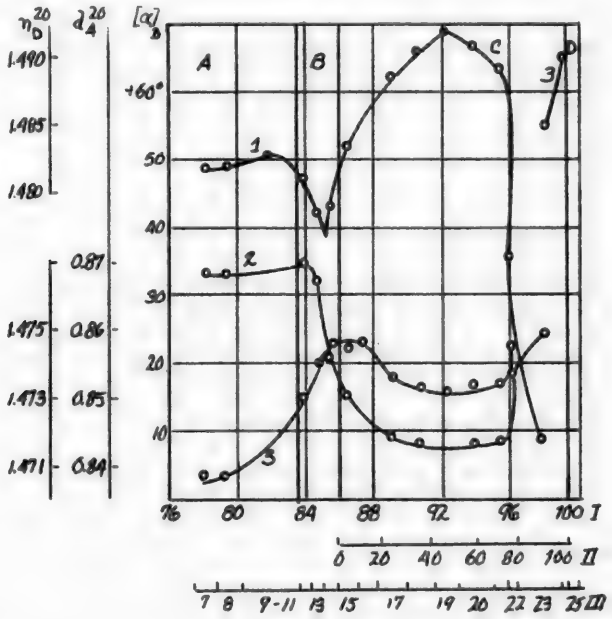
Titanic acid was used as the catalyst [1, 6]. The isomerization of pinene was carried out in the liquid phase with continuous stirring. In the production of an isomerizate containing no pinene, a careful control of the process was carried out in order to stop the reaction as soon as possible when all the pinene had reacted, since a longer heating of the isomerizate with the catalyst would lead to further change of its composition.

Analysis of the Isomerizates

Determination of the amounts of camphene, tricyclene and fenchenes. 1 g of the isomerizate was shaken for 10 minutes with 0.5-1 g (see content of substances determined) of an acid mixture consisting of 90% of 97% HCOOH and 10% of 96-100% H_2SO_4 [7]. 0.15-0.30 ml of water was added and the acids which separated from the solution were removed. After a second washing, the product was completely neutralized and dried with soda. We saponified a weighed portion (0.7-1 g) of the dried substance with a 0.15 N alcoholic solution of NaOH at room temperature for 20 minutes, after which we back-titrated the unreacted NaOH.

Determination of the content of monocyclic terpenes. The content of monocyclic terpenes in the isomerizates was found on the basis of data obtained by an analytic fractionation of the isomerizates with an apparatus of high efficiency.

The data obtained by distillation of one of the isomerizates investigated, which may be considered as typical, are cited in the figure.



Fractionation of an isomerizate containing 46% of unreacted pinene (see Table, Experiment 3).
I) Total distilled (in %); II) Monocyclic terpenes distilled (in %); III) Number of fractions.
1) $[\alpha]_D$, 2) d_4^{20}, 3) n_D^{20}.
A) Pinene and camphene (Fractions 9-11 had a m. p. of 39°); B) Unidentified terpene; C) Monocyclic terpenes; D) Residue from distillation.

Calculation of the pinene content. The pinene content in the isomerizates (B) was determined from the difference, B = 100 − A, where A is the sum of the camphene, tricyclene, fenchenes and monocyclic terpenes found, expressed in percentages.

Since on determination of camphene, pinene is converted by 10% into the ester, the results were divided by 0.90. The results of the camphene determination were corrected in a suitable way.

Determination of the limonene content. The monocyclic terpenes obtained by isomerization of pinene, contain only one optically active component – limonene; therefore, a calculation of the limonene content (b) in each fraction of monocyclic terpenes could be made by the formula

$$b = \frac{[\alpha']_D}{[\alpha'']_D} \cdot 100.$$

where $[\alpha']_D$ is the specific optical rotation of the fraction analyzed, and $[\alpha'']_D$ is the specific optical rotation of the limonene obtained from the original pinene. The results of the determinations of limonene in all the fractions were added up.

In the calculations for $[\alpha]_D$ of limonene we used the $[\alpha]_D$ of the strongest rotating fraction of monocyclic terpenes. The absence in these fractions of admixtures of the optically inactive terpinolene and terpinenes was confirmed by the fact that in the isomerizates which contained above 30% of unreacted pinene (see Table, Experiments 1-4), the strongest rotating fraction of monocyclic terpenes had a similar value $[\alpha]_D$ + 68.8 ± 0.3°, which agreed with the calculated $[\alpha]_D$ + 69.2°. * According to its other properties (d_4^{20} 0.8419- 0.8431, n_D^{20} 1.4730; tetrabromides: optically active forms with m.p. of 105° and racemic form with a m.p. of 125°) this fraction also corresponded to limonene. Limonene with $[\alpha]_D$ +47° was isolated from the isomerizate which contained no pinene and differed from that described only in that it was partially racemized during the reaction.

Determination of the α-terpinene content. The quantitative determination of α-terpinene was carried out by a method which we developed, based on the use of the diene synthesis reaction. 0.5-1 g of maleic anhydride was added to 3-5 ml of the product analyzed. We kept the reaction mixture at room temperature for 3-5 days, stirring it periodically, and washed it with a 3-5% solution of NaOH, dried it with K_2CO_3 and determined α_D. The α-terpinene content in per cent (b) was calculated from the equation

$$b = \frac{\alpha''_D - \alpha'_D}{\alpha''_D} \cdot 100.$$

where α'_D is the optical rotation of the original mixture of terpenes, and α''_D is the optical rotation of the mixture of terpenes after treatment with maleic anhydride. We carried out an analysis of all the monocyclic terpene fractions withdrawn with the fractions having the maximum optical rotation (limonene), and also of some fractions of unidentified terpene (see figure), since we assumed the possibility of the presence of α-terpinene also in these fractions. The results of the analyses were added. By the analyses it was found that α-terpinene was concentrated in the initial fractions of the monocyclic terpenes, where its content reached 10-20%. Only 2-4% of α-terpinene was found in the fractions of unidentified terpene.

Determination of the terpinolene content. The decrease of the optical rotation of the end fractions of monocyclic terpenes was caused by the presence of terpinolene and small quantities of γ-terpinene in them. The calculation of the terpinolene content in the individual fractions obtained on distillation was made from the $[\alpha]_D$ values of these fractions. All the optically inactive terpenes contained in the fractions after the fraction with a maximum optical rotation were considered to be terpinene. The presence of γ-terpinene was neglected in the calculations. This did not lead to significant errors in the analysis of the monocyclic terpenes isolated from isomerizates containing unreacted pinene, since the γ-terpinene content in them was very small. Since the γ-terpinene content in the monocyclic terpenes increased simultaneously with an increase of the α-terpinene content, a somewhat elevated result of the determination of terpinolene (3-5% according to an approximate calculation) was obtained only for the isomerizate which contained no pinene (see Table, Experiment 5).

The richest terpinolene fraction had the following properties: d_4^{20} 0.8617, n_D^{20} 1.4906, tetrabromide with a m.p. of 117°.

* It was calculated from the proportion $\alpha_D = \frac{29.6 \cdot 126}{53}$, where 126° – $[\alpha]_D$ was optically pure limonene [8, 9], 53° – $[\alpha]_D$ was optically pure pinene [10], 29.6° – $[\alpha]_D$ was the initial pinene.

SUMMARY

1. It was demonstrated that, on heating with titanic acid, a direct conversion of pinene to terpinolene, and also of pinene and limonene to α-terpinene occurred, without the formation of limonene as the intermediate product in the first instance and of terpinolene as the intermediate product in the second.

2. The direct conversion of pinene and limonene to α-terpinene without the formation of terpinolene as the intermediate product became apparent only on consideration of the reaction studied from the ionic point of view, i.e., by assuming the formation from pinene (or limonene) of carbonium ion, which was converted further to limonene, terpinolene and the terpinenes.

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Received January 13, 1954.

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* T. p. = C. B. Translation pagination.

POLYMERS OF AMINO ACIDS

(Preliminary Report)

L. N. Akimova and N. I. Gavrilov

In the literature there are repeated indications of an analogy in the properties of polyamino acids and proteins. We tried to observe such an analogy in the behavior of polyamino acids with respect to proteolytic enzymes and in a comparison of their molecular weights with those of the proteins. Moreover, we attempted to find a similarity in the physical properties of the polymers and proteins. Precisely in an attempt to identify the polymers with proteins, we also elucidated the attempt of synthesis of the polymers which was carried out by Woodward and Schramm [1]. In the authors' opinion the polymer which they synthesized was a protein analog. However, in all these investigations and results a simplified and mechanical approach to the most important problem of natural science – the problem of the structure and synthesis of protein – was overlooked.

Studying the action of proteolytic enzymes on polyamino acids of high molecular weight, a number of authors attempted to secure some information of the chemism of the action of these enzymes on proteins [2]. The first enzymatic investigations with polyamino acids were made in 1939 [3]. In these investigations the action of erepsin, papain and tripsin on the water-insoluble polymers of glycine and glycyl-leucine was studied. The enzymes, however, did not act on the polyamino acids. An especially careful fermentation was studied with water-soluble poly-l-lysine. As a result, the extraordinary resistance of such a polymer toward different enzyme systems [4] (carboxypeptidase, pepsin) was recorded. Material on the study of the action of enzymes which cleave proteins, and their capacities to hydrolyze the water-soluble polyamino acids, is exhausted by the foregoing. We assume that even these investigations indicate sufficiently the different structural nature of the polymers, and not only of the proteins, but also of the plasteins obtained synthetically from peptones. In the problem of the similarity and difference of the structure of the proteins and the polymers, the determination of the size of the particles of both is of greatest interest. Moreover, it is necessary to observe that the essential problem of the magnitude of the molecular weight of the polyamino acids has not until now been solved even to a first approximation. Thus, Woodward and Schramm [1] in their first works assumed that the molecular weight of the polymers which they obtained amounted to several millions. Later investigators [3, 5, 6] reduced the assumed size of the polymer molecules considerably, and at present it is necessary to assume it to be close to 6000 (from glycine polymer). Such a striking difference of the sizes of the molecules of polyamino acids from those of proteins and, particularly, the ease of formation of the former, compels us to seek an explanation in the conditions of formation of the molecules. The fundamental difference of a polymerization reaction from that of the synthesis of a protein includes the fact that the synthesis of a protein proceeds in vivo in an aqueous medium, whereas all polymerization reactions take place only in a medium containing traces of water.

Thus, the formation of polyamino acids (organic solvent) is extremely simple compared with that of a protein, the synthesis of which, first, is conditioned by the life process itself; second, requires an unusual medium and, finally, third, the participation of catalysts (enzymes) is required.

Investigations of the physical properties of polyamino acids by means of x-ray structural analysis and spectrophotometry in the infrared region are also of interest. On the basis of the results of these investigations, a large number of authors reached a conclusion concerning the protein nature of the polymers. Thus, by an x-ray investigation of the polyglycine obtained by the polymerization of N-carboxyglycine anhydride, Meyer and Go [5] observed that the fundamental ranges of this polymer lie in areas separated by a distance of 4.15 A. A similar investigation of β-keratin enabled the authors to identify polyglycine with β-keratin. From a comparison of the absorption spectra in the infrared region for the polyamino acids and for the proteins, it was concluded [7] that the definite frequencies characteristic of each amino acid in the polymer are retained also in the proteins which contain these amino acids.

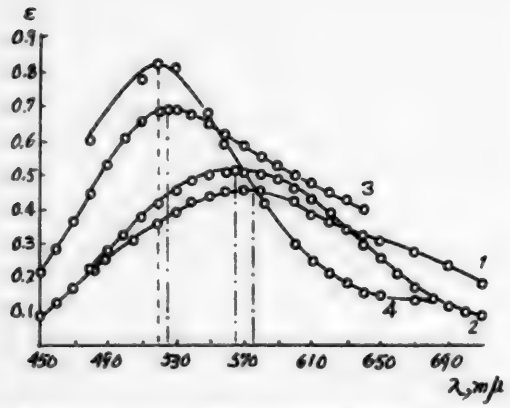

Fig. 1. Spectrophotometric curves of biuret cupric complexes.
1) Tripeptide (1/150 M solution); 2) gelatin (0.25% solution); 3) polyglycine (0.14% solution); 4) tetrapeptide (1/150 M solution).

A series of authors [8] used polyglycine as a model for the determination of the quantity of water absorbed by protein for one peptide bond at different relative humidities. The absorption of water by the polyglycine polymer obtained by two different methods was the same in spite of their different average molecular weights; but this absorption of water by both glycine polymers [6, 9] considerably exceeded the absorption by tetra-, penta- and hexa- glycine, which should be expected from the point of view of a change of the quantity to a new character. Moreover, the quantity of absorbed water calculated for 1 mole of the polymer on the basis of the number of free amine and ester groups, was considerably less than the observed value. Owing to the fact that silk absorbs the same quantity of water as polyglycine, the authors concluded that there is a different number of polar groups in the structure of the silk and in that of polyglycine.

Proceeding from the above-cited observations, it seemed to us also that the forces which control the synthesis of the polyamino acids are probably similar to those which lead to the organization of a large protein molecule. However, from the very beginning, our investigations of the polymers showed that we were incorrect in our assumption that, not only the molecular weight and a number of physical properties (solubility, etc.) distinguished the proteins from the polyamino acids, but that also the structure of these molecules themselves differed basically from each other.

The biuret reaction, so characteristic of proteins, showed the definite presence of peptide structures both in proteins and in the polyamino acids. Visually, the cupric complexes of polyamino acids hardly differ in color from those of the proteins, particularly the protamines. However, a spectrophotometric investigation of the cupric complexes of the peptides of proteins and polyamino acids (Fig. 1) indicated their essential difference which, obviously, also depended on the internal structure of the molecule.

As is known, the spectrophotometric curves of solutions of the biuret cupric complexes of proteins have an absorption maximum in the wavelength range of 540-565 mμ. The determination of copper in the cupric complexes of proteins [10], and the total course of the curve of these complexes with a characteristic maximum, forces us to assume as correct the hypothesis which we put forth earlier concerning the tripeptide nature of the structure of the linear portion of the protein structure. The spectrophotometric curves of glycine polymers obtained by different methods, unlike those of the proteins, have an absorption maximum at 525 mμ. This fact relates the cupric complexes of the polymers to those of the octa- and tetra- peptide (maximum 520-525 mμ) [11]. Like the proteins, the copper number of which indicated their tripeptide character, the determination of copper in the cupric complexes of the polymers corresponded to their tetrapeptide content (accordingly, octapeptide; Table 2).

In spite of such a completely expected similarity, the absorption spectrum of polyglycine also has an essential difference from that of the octapeptide (or tetrapeptide) (Fig. 2). This difference includes the fact that in the long-wave part of the spectrum of about 610-620 mμ we have considerable light absorption which, being superimposed on the fundamental red color, gave a visual violet color.

What are the considerations which condition the increase of light absorption in this region? We offer the following tentative hypotheses:

1) water of hydration, undoubtedly present in the polyamino acid molecule, and possibly bound with definite, regularly recurring structures, gives a condition for the formation of the additional absorption of such an intricate complex. It is necessary to observe that not only the absorption maximum at 525 mμ indicates the characteristic octa-tetrapeptide structure of such a complex, but also the copper number determined by the whole structure of the complex indicates the presence of octapeptide fragments in the polymers;

2) the increase of the intensity of light absorption in the long-wave region, i.e., in the 610-620 mμ region, indicates the presence of some additional groups, close in their character to dipeptide, which affect this increase (the absorption maximum of the dipeptides is at 610 mμ). Such an intensity increase was explained by one of us

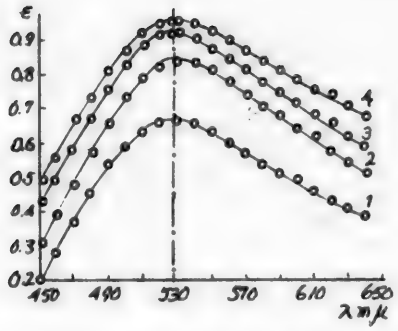

Fig. 2. Spectrophotometric curves of biuret cupric complexes of 0.14% solutions of glycine polymers obtained under different conditions.
1) In water; 2) in organic solvent; 3) in presence of enzyme; 4) in production of diketopiperazine.

(N. I. Gavrilov) by the possible existence in the polyamino acid structures of dipeptide fragments, which are not fragments of the main polymer chain. By analogy with starch, they may represent side chains to the basic valence chain of the polymer. The empirical formula of any polymer is packed into a tetrapeptide fragment of anhydride arrangement. According to analytical data, and to the absorption maximum of its copper complex, the glycine polymer which we obtained corresponded to the octapeptide. We can represent the structure of such a polymer as an octapeptide with a molecular weight of 474, combined n times $(C_{16}H_{26}O_9N_8)_n$.

The presence of the piperazine ring in the structure of a protein seems to be most important in conditioning its physiological functionality. All proteins contain approximatedly from 25-40% of the cyclic forms of bonds (from α-amino nitrogen) between the amino acids. And it is natural that, in the first place, we attempted to find these forms of bonds also in the polyamino acids. The picric reaction, observed by a whole series of investigators for polyamino acids, did not appear to be their structural reaction, because the anhydride reaction was absent after treatment of a majority of the polyamino acids with hot water (with the exception of the polymer obtained in an organic solvent). It is necessary to note again that the washing filtrates, from the treatment of the polyamino acids with water, developed a red biuret reaction, which indicated the presence in them of tetrapeptides or peptides of multiple length.

Experiments with the electroreduction of the polyamino acids showed a complete absence in their structure of the cyclic form of bonds of the amino acids. The polyamino acids were not fermented by pepsin. Thus, it was now possible to state definitely that the structure of the polyamino acids differed essentially from the protein structure. This difference was so great that it was impossible even to consider the polyamino acids as protein-like compounds. Nevertheless, clarification of their structure, and especially establishment of the order and character of the reactions leading to their formation, may also shed light on the structure of protein.

EXPERIMENTAL

N-carboglycine anhydride (Leuchs' anhydride) [12] was used for the production of the glycine polymers.

1. Synthesis of N-Carboglycine Anhydride *

6.3 g of carbobenzoxyglycine with 35 ml of anhydrous ether, and 6.7 g of powdered PCl_5 was shaken, with cooling, until all had dissolved (approximately 20 minutes). The liquid, filtered at reduced pressure and 10°, was evaporated until the formation of a viscous oil as the residue, which was treated twice with dry petroleum ether. On the addition of a third portion of petroleum ether, and on cooling to −10°, the oil crystallized. The substance which formed was filtered off and washed with ether and with alcohol. According to the analysis it was the inner anhydride of N-carboglycine. Its yield was 2.7 g.

2. Production of the Glycine Polymers

a) In water at room temperature. A twofold quantity of water (2 ml) was added to 1.0 g of carboglycine anhydride, obtained by the above-described method; moreover, strong frothing and evolution of CO_2 resulted. After 10 minutes the precipitate was filtered off and washed on the filter, first with cold water (in the aqueous filtrate there was a red biuret reaction and a negative anhydride reaction), and then with hot water (in the filtrate there was a violet biuret reaction and a negative anhydride reaction). We continued the treatment of the precipitate with boiling water until there was a negative biuret reaction in the filtrate, after which the precipitate was washed with alcohol.

* It is best to obtain Leuchs' anhydride by a method described for the acid chloride of carbobenzoxyglycine. As shown experimentally, an increase of the quantities of the starting materials by a factor of 2 reduced the yield by a factor of 2.

Found %: C 40.20, 39.92; H 5.66, 5.83; N 22.24, 22.19 $(C_{16}H_{26}O_9N_8)_n$. Calculated %: C 40.51; H 5.49; N 23.62.

Properties. It was insoluble in boiling water, organic solvents and glacial acetic acid. It dissolved in concentrated hydrochloric and in 100% formic acids. On 30-minute standing with $CuCl_2$ and NaOH, it gave a positive biuret reaction of a violet color. The anhydride reaction was negative.

The aqueous filtrates from the treatment of the polymer with boiling and with cold water were concentrated to dryness in vacuo. With a stream of cold water, the residue was transferred to a beaker. In addition, the polymer precipitate which came down was filtered off. The filtrate was precipitated with alcohol, and the precipitate was filtered off and washed on the filter with alcohol. The resulting substance was readily soluble in water, and insoluble in alcohol. It gave a biuret reaction with a red hue.

Found %: C 37.29, 37.37; H 6.30, 6.06; N 21.72, 21.68. $C_6H_{11}O_4N_3$. Calculated %: C 38.00; H 5.9; N 22.2. $C_8H_{14}O_5N_4$. Calculated %: C 39.97; H 5.69; N 22.6.

On comparison of the properties and analytical data of this substance with those of the tri- and tetrapeptides, it followed that the substance which we isolated was a mixture of the tri- and tetrapeptides of glycine (an admixture of peptides of greater length was also possible).

b) In an organic solvent with heating. 20 ml of xylol was added to 1.7 g of N-carboglycine anhydride, and it was heated with Wood's alloy for 45 minutes. The decomposition of the anhydride and, as a result of this decomposition the formation of the polymer, took place only at 100°, and therefore only a solvent with a b.p. of 100° or more could be used for this purpose. On completion of the reaction (after 45 minutes), the precipitate was filtered off and washed with xylol. Completion of the reaction was judged by the cessation of the evolution of CO_2 (by reaction with baryta water). The polymer yield was 0.9 g, i.e., it was quantitative. The substance was treated with boiling water for analysis.

Found %: C 40.41, 40.50; H 5.70, 5.74; N 23.16, 23.19. $(C_{16}H_{26}O_9N_8)_n$. Calculated %: C 40.51; H 5.49; N 23.62.

Properties. It was insoluble in boiling water, organic solvents and glacial acetic acid; it was poorly soluble in concentrated hydrochloric acid; it was soluble in 100% formic acid on heating; it dissolved in alkali only on standing for several hours in the presence of copper. The biuret reaction was of a violet color. The anhydride reaction was positive.

c) Investigation of the polymer isolated in the synthesis of diketopiperazine. In the synthesis of diketopiperazine from the hydrochloride of the methyl ester of glycine and NaOH, according to Fischer a glycine polymer was isolated as a by-product. The treatment of this polymer was similar to that described in Experiments "a" and "b".

Properties. It was insoluble in boiling water, organic solvents and glacial acetic acid; it was insoluble in alkali and dissolved in it only on addition of a copper solution, upon which a red biuret reaction appeared instantly; it was soluble in concentrated hydrochloric and in 100% formic acids in the cold. The biuret reaction was positive; the anhydride reaction, with long heating, was negative. The analytical data of such a polymer yielded uncertain results. *

3. Investigation of the Structure of the Glycine Polymers

a) Electroreduction of the polymer obtained in an aqueous medium (carried out by P. G. Ioanisian). 0.1038 g of polyglycine was dissolved in 100 ml of concentrated hydrochloric acid, and 60 ml of distilled water and approximately 30 ml of concentrated hydrochloric acid (washing) were added. The temperature of the solution did not rise above 25°, and after external cooling it fell to 11-12°, and then during the electroreduction rose to 25°. The electroreduction was continued for 7 hours. The reduced polymer, together with the washing waters, was concentrated in vacuo to a small volume. The residue was boiled under reflux with 40 ml of concentrated hydrochloric acid for 20 hours. After the acid hydrolysis the solution was concentrated to dryness in vacuo. Several drops of 20% alkali, and then 0.2 N NaOH, was added to the residue in the flask until there was a neutral reaction to neutral red. Then, adding 10 ml of a formol mixture, it was back-titrated according to Sörensen-Gavrilov.

0.1038 g sub.: 14.32 ml 0.1 N H_2SO. Found %: NH_2-group 19.31. 0.1038 g sub.: 14.54 ml 0.1 N H_2SO_4. Found %: N 19.61.

* It is probably a mixture of polymers of different length.

The equality of the quantity of amine nitrogen after reduction (19.31%) and the total nitrogen (19.61%) indicated the absence of piperazine in the reduction products.

b) Determination of the amine nitrogen in the polymer obtained in water. Because the polymer was soluble in 100% formic acid in the cold, it was of interest to carry out a determination according to Slyaik with this acid as the solvent. By the determination, it was found that formic acid decomposed the nitrous acid and, therefore, we were unable to make a determination of the amine groups of the polyglycine. A determination of the amine nitrogen in dilute (15%) hydrochloric acid also led to no satisfactory results.

As has already been mentioned, one of the most interesting characteristics of the polymers was their molecular weight. In such compounds as polyamino acids, particularly the glycine polymer, a determination of the molecular weight may be carried out on the basis of a quantitative calculation of the end amine groups. The methods of Sörensen and Slyaik are not very reliable, as a result of the difficult solubility of the polymer, and the impossibility of finding suitable conditions for determination of the amine groups. Following Experiment "3b", we decided to carry out an amine nitrogen determination in the polymer with hydrochloric acid, by the equivalent free amine groups after esterification of the polymer with ethyl alcohol.

c) Esterification of the polymer (obtained in water). 25 ml of anhydrous ethyl alcohol was added to 0.75 g of the polymer, and saturated with dry hydrogen chloride for 2.5 hours in the cold, and then for 3 hours with heating. The precipitate did not dissolve. After cooling, the precipitate was filtered off, washed with alcohol and dried over alkali and calcium chloride in a vacuum-desiccator. The substance, containing halide, was analyzed for its amine nitrogen content according to Sörensen-Gavrilov.

0.3660 g sub.: 5.08 ml 0.1 N NaOH. 0.3660 g sub.: 5.35 ml 0.1 N H_2SO_4. Found %: C 40.17, 40.26; H 5.80, 5.90; N 20.93. $C_{18}H_{30}O_9N_8 \cdot HCl$. Calculated %: C 40.12; H 5.75; N 20.80.

The quantity of hydrochloric acid found was equal to 5.3%, which corresponded to 2.1% amine nitrogen in the polymer. The amine nitrogen, calculated for the hydrochloride ester of the octapeptide, amounted to 2.6%.

d) Preparation of cupric biuret solutions of the polymers. 15 ml of a 2% solution of $CuCl_2$ and 15 ml of a 2% solution of NaOH were added to a weighed portion of 100-150 mg of the polymer. The solution was mixed by shaking for from 1 hour to several hours (in the case of the polymer obtained in the organic solvent), and was centrifuged after a definite time. The clear solution of the copper complex of the polymer was used for spectrophotometry. 0.14% solutions (according to the polymer) of the cupric complexes were usually prepared. We used an SF-4 spectrophotometer for taking the spectrophotometric curves. The results of the spectrophotometry of the polymer complexes obtained under different conditions are presented in Table 1 and Fig. 2.

e) Determination of copper in biuret cupric solutions of polymers. The biuret cupric solution of the polymer was centrifuged and from 10 to 30 ml of the clear solution of the copper complex, containing from 50 to 150 mg of the original polymer, was used. After decomposition of the copper complex with 2N sulfuric acid * the copper in the solution was determined iodometrically (Table 2).

The theoretical copper number for the octapeptide (tetrapeptide) was equal to 246. The experimental values of the copper number of the polymers were equal to 236 on the average.

4. Production of Polymers in the Presence of Gastric Juice

The activity of gastric juice on plastein formation was verified on Witte peptone. For this, 3 g of the peptone was dissolved in 9 ml of water. A pH of 4.5 was assumed to be the optimum condition of the medium for plastein formation. 20 ml of gastric juice was added for reduction of the pH of the peptone solution from 7.5 to 4.5. After 1 hour of standing in a thermostat ** a precipitate came down, which was centrifuged; the solution was decanted, and it was washed 2 times with water. The precipitate gave a biuret reaction of a protein nature (without traces of red), whereas the solution which was poured off from the precipitate gave only a red biuret reaction. Plastein formation proceeded much faster with the action of gastric juice on an aqueous solution of the peptone than with the action of pepsin on the peptone solution.

* Determination of the copper in solution was made both before and after combustion with H_2SO_4. The results of the determinations agreed. Regeneration of the polymer took place on decomposition of the copper complex with sulfuric acid.

** An appreciable turbidity was observed on addition of a completely clear gastric juice to a well-centrifuged aqueous solution of the peptone.

TABLE 1

Spectrophotometric Curves of 0.14% Solutions of Biuret Cupric Complexes of Different Polymers

λ (in mμ)	Values of the optical densities					
	aqueous polymer	polymerization in the presence of			polymer obtained in organic solvent	polymer of diketopiperazine
		gastric juice, unneutralized	gastric juice + CH_3COONa	gastric juice + glycine		
450	0.213	0.210	0.179	0.202	0.185	0.209
460	0.284	0.281	0.254	0.286	0.258	0.278
470	0.371	0.374	0.340	0.381	0.343	0.360
480	0.461	0.473	0.430	0.478	0.439	0.447
490	0.544	0.561	0.505	0.561	0.534	0.524
500	0.611	0.633	0.572	0.636	0.607	0.591
510	0.661	0.689	0.620	0.690	0.654	0.647
520	0.681	0.713	0.642	0.719	0.695	0.677
525	**0.693**	**0.727**	**0.658**	**0.736**	**0.695**	**0.690**
530	0.683	0.722	0.655	0.733	0.683	0.686
540	0.677	0.707	0.651	0.731	0.666	0.679
550	0.634	0.676	0.636	0.722	0.643	0.663
560	0.617	0.656	0.597	0.672	0.610	0.630
570	0.586	0.624	0.569	0.640	0.583	0.591
580	0.553	0.589	0.540	0.608	0.554	0.556
590	0.525	0.557	0.517	0.579	0.537	0.516
600	0.501	0.523	0.492	0.549	0.515	0.474
610	0.481	0.496	0.466	0.516	0.505	0.430
620	0.447	0.458	0.440	0.481	0.488	0.391
630	0.431	0.427	0.412	0.447	0.469	0.360
640	0.399	0.392	0.384	0.411	0.433	0.315

TABLE 2

Copper Numbers of the Polymers

Origin of polymer	Conditions of formation of copper complexes	Quantity of polymer (in g)	ml 0.05 N solution of $Na_2S_2O_3$ consumed	Copper number
obtained in water	deficiency of copper	0.0573 in 22 ml	4.7	249.7
obtained in water	ordinary conditions	0.0294 in 15 ml	2.65	221.7
obtained in water	ordinary conditions	0.0261 in 10 ml	2.35	222.1
obtained in water	ordinary conditions	0.0507 in 25 ml	4.61	220.3
obtained in water	after 1 day of standing with 10% solution of NaOH	0.0718 in 20 ml	4.80	299.3
polymer hydrochloride from Experiment "c"	ordinary conditions	0.0784 in 25 ml	6.76	233.3
from Leuchs' anhydride in an organic solvent	weighed portion dissolved in conc. HCl. Added: 2% $CuCl_2$ and 20% NaOH, with cooling	0.0445 in 15 ml	3.8	234
from Leuchs' anhydride in an organic solvent	cupric complex prepared by usual method and left overnight with $Cu(OH)_2$	0.0949 in 30 ml	7.6	262.8
polymer of diketopiperazine	ordinary conditions	0.0651 in 15 ml	5.22	249.3
polymer obtained from Leuchs' anhydride in a gastric juice medium	ordinary conditions	0.1464 in 15 ml	11.97	244.0
polymer obtained from Leuchs' anhydride in a gastric juice medium	ordinary conditions	0.0976 in 10 ml	8.12	240.4

Production of the polymers. Similar polymer precipitates were obtained by the action of gastric juice on Leuchs' anhydride without the introduction of buffer, and also with the establishment of a pH of 4.5 by means of sodium nitrate and glycine.

We conducted the following experiment in order to elucidate the mechanism of formation of the polymers (whether it proceeds via the stage of cyclization of the tripeptide to N-glycine diketopiperazine, or whether it is connected with a linear polymerization of a chain character). Assuming that one of the intermediate stages in the synthesis of the polymers was the formation of diketopiperazine or its derivative, we decided to accelerate the polymerization process. For this we added diketopiperazine at the moment of formation of the polymer from Leuchs' anhydride. 2 g of Leuchs' anhydride was added to the solution containing 0.15 g of diketopiperazine in 4 ml of water. 5 minutes after addition of the anhydride strong frothing and evolution of CO_2 began, which was stopped after 15 minutes. The precipitate was filtered off and treated, first with cold, and then with hot, water. Moreover, the yield of the polymer was 1.1 g, i.e., it was quantitative. 0.12 g of diketopiperazine was separated from the filtrate by concentration. The diketopiperazine which obviously did not take part in this reaction, was recovered as a result of the reaction carried out.

Discussion of Results

The principal difference in the behavior and properties of proteins and the polymers can be observed on the basis of the investigation made. This difference includes the facts that:

1) in all proteins studied thus far; from 25 to 40% of the amino acids are cyclized to piperazines;

2) the investigation of the absorption spectra of the cupric biuret complexes of the proteins indicated the predominance of "violet" complexes (46-85%) in their structure [10]; "red" copper complexes comprised only a small per cent in protein (15-54%);

3) in the vast majority of cases the proteins have the capacity to dissolve in water (albumins), in alcohol (glutelins), and in concentrated salt solutions (globulins), whereas the polymers are insoluble in these solvents, and dissolve with difficulty in concentrated acids and alkalis.

The polymers differ sharply from the proteins by the following:

1) the complete absence of cyclic forms of bonds between the amino acids; only in the polymer formed in an organic solvent (xylol) did we observe a negligible presence of cyclic forms of bonds, not exceeding 8%;

2) the polymers contained, depending on the length of the peptide, up to 2% of amino nitrogen, whereas the proteins did not have end α-amino acid groups.

The cupric biuret complexes were the most interesting of all the properties of the polymers. An analysis of the absorption spectra of the cupric biuret complexes of the polymers indicated their great difference from the proteins. The absorption spectra of the cupric complexes of the proteins were characterized by the presence of those structures which give complexes with copper, formed by four nitrogen atoms (on the average 30%), and are characterized by a quite definite absorption maximum (540-565 mμ), with a very sharp reduction of the intensity of absorption in the long-wave region.

An analysis of the absorption spectra by the cupric complexes of the polymers quite definitely indicated the existence of a fundamental maximum at 525 mμ, with considerable absorption in the long-wave region, which also affected the visual color of these solutions (violet).

Whereas the copper number of the proteins quite clearly showed the tripeptide character of the individual fragments, the cupric complexes of the polymers differed exactly by tetrapeptides and peptides, by a multiple of 4 (8-, 12-, 16-, etc.). The polyglycine from Leuchs' anhydride which we studied was an octapeptide. Since it differed from the synthetic octapeptide in solubility and in the absorption spectra of the cupric complexes, it is necessary to assume that it underwent further association to a molecule of considerable size.

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Received March 15, 1954

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* T. p. = C. B. Translation pagination.

THE ALKALOIDS FROM SOPHORA PACHYCARPA

A NEW ALKALOID – PACHYCARPIDINE

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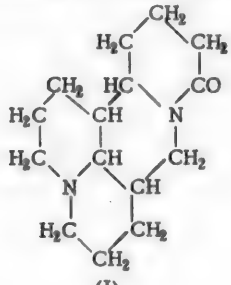
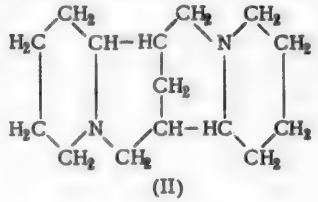
Sophora pachycarpa, thick-pistilled Sophora (bean family), is an alkaloidal plant which is widely distributed in Central Asia, the study of which was begun in 1933 by A. P. Orekhov and his coworkers. The new alkaloid, sophocarpine, and the earlier-described matrine (I) were isolated from the seed of this plant by Orekhov and Proskurnina [1]. Together with sophocarpine and matrine, a new alkaloid, pachycarpine (II), which is apparently the dextrorotatory form of lupinidine, was isolated from the stems and leaves of Sophora pachycarpa by Orekhov, Rabinovich and Konovalova [2].

In connection with the introduction of pachycarpine to medical practice, the attention of investigators has again been focused on the chemical study of this widely available plant, the total alkaloid content of which amounts to 2-2.5% of its dry weight. In 1953 Proskurnina and Kuzovkov [3] isolated still another crystalline alkaloid – sophoramine, described earlier as a base from Sophora alopeeuroides – from the above-ground parts of thick-pistilled Sophora. They established that sophocarpine and sophoramine form matrine on catalytic reduction. Thus, the alkaloids of Sophora pachycarpa isolated until now belong to two different heterocyclic systems.



(I)



(II)

By further study of the alkaloids of thick-pistilled Sophora by using the ion-exchange adsorption method, we were able to separate from an aqueous extract of the plant one more crystalline base with a m. p. of 177-179°, $[\alpha]_D$ + 26.6°, which forms a crystalline picrate with a m. p. of 210-211° and a crystalline pechlorate with a m. p. of 204-205°. According to an elementary analysis of both the base and its salts, the composition of the base $C_{15}H_{22}N_2O_2 \cdot H_2O$ was established. Since the newly isolated alkaloid differed in its properties from the bases described in the literature, we named it pachycarpidine.

Pachycarpidine was readily reduced by zinc dust in sulfuric acid solution, forming an oxygen-free liquid base, desoxypachycarpidine, from which the following were obtained: a crystalline picrate of composition $C_{15}H_{22}N_2 \cdot (C_6H_3O_7N_3)_2$ with a m. p. of 128-130°, and a hydriodide of composition $C_{15}H_{22}N_2 \cdot HI \cdot H_2O$ with a m. p. of about 280°.

Such a simple formation of an oxygen-free substance, together with the absence in pachycarpidine of hydroxyl, methoxyl and N-methyl groups, enabled us to assume that both nitrogen atoms of this alkaloid occur in the form of oxide groupings similar to those which occur in trilupine [4]. This assumption was confirmed by the production of the original pachycarpidine from desoxypachycarpidine by oxidation with hydrogen peroxide.

EXPERIMENTAL

Isolation of Pachycarpidine

2 kg of the above-ground parts of the plant was drenched with a 2% solution of sulfuric acid. After 18-20 hours the extract (as a viscous syrup) was diluted with an equal volume of water, after which it was filtered through a

column filled with Espatite-I, first converted to the H^+-form. Moreover, the alkaloids were completely absorbed by the H^+-cationite. The desorption of the alkaloids was carried out with a 20% solution of ammonia in methyl alcohol. After vacuum evaporation of the resulting filtrate the residue was dissolved in 10% sulfuric acid. The acid solution was washed repeatedly with benzene in order to remove the resinous, weakly-basic impurities, then it was saturated with a 40% solution of sodium hydroxide, and extracted with chloroform. After evaporation of the solvent the residue crystallized; 16 g of a crystalline, slightly oily base was obtained, which was readily soluble in water, insoluble in ether, and difficultly soluble in acetone. After dissolving it in hot acetone (1:20), and after evaporation of the latter to 1/3 of its original volume, the pachycarpidine crystallized. During the determination of the melting point the base melted at 140-150°, then solidified again and melted at 177-179°.

Pachycarpidine was also isolated by extraction of the above-ground parts of Sophora pachycarpa with isopropyl alcohol. The alkaloids obtained from 1 kg of the plant were dissolved in dilute sulfuric acid, and after treatment with benzene the acid solution was saturated with a 40% solution of sodium hydroxide, extracted with ether, and then extracted with chloroform. 12 g of pachycarpidine was isolated from the ether fraction and 7 g of pachycarpidine was obtained from the chloroform fraction; $[\alpha]_D$ + 26.6°.

3.057 mg sub.: 7.128 mg CO_2; 2.350 mg H_2O. 4.568 mg sub.: 10.711 mg CO_2; 3.581 mg H_2O. 6.965 mg sub.: 0.637 ml N_2 (23.0°, 739 mm). 8.150 mg sub.: 0.733 ml N_2 (24.0°, 738 mm). Found %: C 63.59, 63.94; H 8.60, 8.77; N 10.25, 10.05. $C_{15}H_{22}N_2O_2 \cdot H_2O$. Calculated %: C 64.2; H 8.57; N 10.0.

Salts of Pachycarpidine

The picrate was formed as an oily residue by mixture of alcoholic solutions of the base and picric acid. After recrystallization from ethyl acetate its m. p. was 210-211° (with decomp.).

4.650 mg sub.: 8.740 ml CO_2; 2.219 mg H_2O. 3.411 mg sub.: 6.444 mg CO_2; 1.551 mg H_2O. 3.950 mg sub.: 0.520 ml N_2 (23°, 735 mm). 5.590 mg sub.: 0.718 ml N_2 (24.5°, 738 mm). Found %: C 51.26, 51.52; H 5.33, 5.09; N 14.65, 14.30. $C_{15}H_{22}N_2O_2 \cdot C_6H_2(OH)(NO_2)_3$. Calculated %: C 51.32; H 5.09; N 14.2.

The perchlorate was formed as an oily powder by mixture of a solution of the base in 10% hydrochloric acid and a saturated aqueous solution of sodium perchlorate. After recrystallization from 96% alcohol (1:10) the perchlorate was obtained as fine needles with a m. p. of 204-205° (with decomp.), depressed to 180°).

3.320 mg sub.: 6.022 mg CO_2; 1.810 mg H_2O. 4.061 mg sub.: 7.424 mg CO_2; 2.339 mg H_2O. 7.120 mg sub.: 0.493 ml N_2 (24.5°, 744 mm). 4.115 mg sub.: 0.249 ml N_2 (23°, 745 mm). 7.633 mg sub.: 3.031 mg AgCl. 5.673 mg sub.: 2.352 mg AgCl. Found %: C 49.47, 49.85; H 6.10, 6.44; N 7.81, 7.94; Cl 9.82, 9.74. $C_{15}H_{22}N_2O_2 \cdot HClO_4$. Calculated %: C 49.72; H 6.35; N 7.73; Cl 9.8.

Reduction of Pachycarpidine

3 g of zinc dust was added gradually (during 1 hour) to a solution of 3.3 g of pachycarpidine in 20 ml of 10% sulfuric acid, with mechanical stirring. After 1.5-2 hours the excess of zinc dust was filtered off, and the filtrate was saturated with a 40% solution of sodium hydroxide and extracted with ether. 2.6 g of desoxypachycarpidine, as a light, mobile oil, remained after evaporation of the ether.

Salts of Desoxypachycarpidine

The picrate was formed as an oil by mixture of alcoholic solutions of the base and picric acid. On addition of acetone the picrate was converted to a solution from which, on standing, it crystallized; its m. p. was 128-130°.

4.160 mg sub.: 7.090 mg CO_2; 1.468 mg H_2O. 3.609 mg sub.: 6.172 mg CO_2; 1.323 mg H_2O. 4.245 mg sub.: 0.622 ml N_2 (23°, 745 mm). 4.030 mg sub.: 0.586 ml N_2 (23.0°, 745 mm). Found %: C 46.48, 46.64; H 3.95, 4.13; N 16.56, 16.43. $C_{15}H_{22}N_2 \cdot [C_6H_2(OH)(NO_2)_3]_2$. Calculated %: C 47.09; H 4.06; N 16.27.

The hydriodide was obtained as a yellowish powder by the addition of hydriodic acid to a solution of the base in acetone.

Its m. p. was ~280° after recrystallization from 96% alcohol.

8.256 mg sub.: 13.26 ml 0.01 N $Na_2S_2O_3$. 6.745 mg sub.: 10.73 ml 0.01 N $Na_2S_2O_3$. Found %: I 33.98, 33.66. $C_{15}H_{22}N_2 \cdot HI \cdot H_2O$. Calculated %: I 33.77.

Oxidation of Desoxypachycarpidine

0.35 g of the base was mixed with 2 ml of a 27% solution of H_2O_2 and 2 ml of water. The base dissolved after

standing for 3 days, and the excess H_2O_2 was removed in vacuo. The residue was dissolved in chloroform, the extract was dried, and the solvent was removed. The resulting base crystallized on treatment with acetone. A sample of a mixture of the resulting base with pachycarpidine showed no melting point depression.

SUMMARY

1. A new crystalline alkaloid, named pachycarpidine, of composition $C_{15}H_{22}N_2O_2 \cdot H_2O$, was isolated from the above-ground part of Sophora pachycarpa (thick-pistilled Sophora).

2. By reduction of pachycarpidine with zinc dust in sulfuric acid solution, an oxygen-free base $C_{15}H_{22}N_2$ was obtained, which on oxidation with hydrogen peroxide yielded the original pachycarpidine.

3. Both of the oxygen atoms of pachycarpidine occurred as N-oxide groupings.

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Received April 23, 1954

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SYNTHESIS OF ORGANO-ELEMENTARY COMPOUNDS OF THE ALIPHATIC SERIES BY THE DIAZO METHOD

VI. SYNTHESIS OF COMPOUNDS OF THE ELEMENTS OF GROUP V – ORGANOPHOSPHORUS COMPOUNDS. TRICHLOROMETHYLPHOSPHINIC ACID AND ITS DERIVATIVES

A. Ya. Yakubovich and V. A. Ginsburg

In a previous report [1] it was shown that the reaction of aliphatic diazo compounds with the phosphorus halides can serve as a convenient method of synthesis of the α-alkyl halide derivatives of phosphorus. For example, chloromethyldichlorophosphine was obtained in this way.

On attempt to obtain phosphorus chloromethyltetrachloride from it by chlorination in CCl_4 in the cold with an excess of chlorine, it was found that the resulting product was not the substance expected, but was a compound of a composition corresponding to the formula CCl_3PCl_4.

Thus, the reaction of chloromethyldichlorophosphine with an excess of chlorine proceeded according to the scheme:

$$ClCH_2PCl_2 \xrightarrow{Cl_2} ClCH_2PCl_4 \xrightarrow{Cl_2} Cl_2CHPCl_4 \xrightarrow{Cl_2} Cl_3CPCl_4.$$

The bromination reaction of $ClCH_2PCl_2$, which can be stopped easily at the chlorobromomethyldichlorodibromophosphoric derivative $ClBrCHPCl_2Br_2$ stage, proceeds exactly the same, but more slowly.

Such ease of chlorination of the chloromethyldichlorophosphine organic radical is explained, on the one hand, by the presence of a chlorine atom in the methyl group which, apparently, is chlorinated more readily than the unsubstituted group, as was also observed, for example, for the methylsilanes [2]; on the other hand, apparently, it is essential that the chlorination of the organic radical in this case proceed in the presence of the $RPCl_4$ compound which, like PCl_5, can catalyze the chlorination process.

The more readily proceeding halogenation of the alkyl radical of the chloromethyldichlorophosphine enabled us also to obtain and to investigate a series of perchloromethyl organophosphorus compounds which were unknown before the beginning of our investigation. Since an acquaintance with the properties of the series of compounds indicated revealed interesting peculiarities in their chemical behavior, a more detailed investigation of these substances was undertaken.

Phosphorus dichloromethyltetrachloride was obtained by the chlorination of chloromethyldichlorophosphine with the calculated quantity of chlorine. This substance was a crystalline compound which was difficultly soluble in CCl_4, and which decomposed on heating. On hydrolysis, hygroscopic dichloromethylphosphinic acid was formed, which was isolated as the monohydrate with a m. p. of 53° (after careful drying – m. p. 115°).

Phosphorus trichloromethyltetrachloride was obtained by chlorination of $ClCH_2PCl_2$ with an excess of chlorine. This consisted of colorless crystals, which dissolved poorly in organic solvents. The substance dissolved slowly in cold water or in a 0.5 N aqueous solution of potassium hydroxide, during which its hydrolysis did not proceed completely; a 1-2 hour boiling of a weighed portion of the substance in an excess of 0.5 N potassium hydroxide led to the splitting off of all seven chlorine atoms of the molecule. By treatment of the tetrachloride with sulfurous anhydride, it was converted to the acid dichloride of trichloromethylphosphinic acid, which was a hygroscopic solid substance, characterized by still greater stability toward hydrolysis.

This acid chloride hydrolyzed very slowly in cold water, and in aqueous 0.5 N caustic potash, for which titration of the hydrolyzate indicated the splitting off of only one halide atom.

Boiling of the substance with alkali for 1-2 hours led to the complete decomposition of the molecule and to the splitting off of all five chlorine atoms.

The low mobility of the second chlorine atom of the acid chloride in this compound appeared also in the production of the anilides. In benzene solution the acid dichloride and aniline readily yielded the monoanilide $CCl_3PO(Cl)NHC_6H_5$. Long (3-5 days) standing of a mixture of CCl_3POCl_2 with an excess of aniline in benzene was necessary for production of the dianilide.

On production of the esters of trichloromethylphosphinic acid by the usual methods, there can be a risk of cleavage of the C–P bond, which may proceed by the action of sodium alcoholate, similar to that which occurred in the series of organosilicon compounds, which readily split off the trichloromethyl group by the action of aqueous alkalies and even water [2]; therefore, the reaction of its acid chlorides with ethyl nitrite was used for production of the ethyl ester of trichloromethylphosphinic acid, for which it was assumed that reaction proceeded according to the scheme:

$$CCl_3POCl_2 + 2C_2H_5ONO \rightarrow CCl_3PO(OC_2H_5)_2 + 2ClNO.$$

However, even under the conditions of a large excess of ethyl nitrite the replacement of halides by the ethoxyl group did not take place completely; therefore, for the purpose indicated above the reaction of ethyl nitrite with CCl_3PCl_4, was studied, as a result of which the diethyl ester of trichloromethylphosphinic acid was obtained according to the reaction:

$$CCl_3PCl_4 + 3C_2H_5ONO \rightarrow CCl_3PO(OC_2H_5)_2 + 3ClNO + C_2H_5Cl.$$

The diethyl ester of trichloromethylphosphinic acid was a colorless liquid with a fruity odor, was readily soluble in organic solvents and was poorly soluble in water. By saponification of the indicated ester by heating at about 150° in a sealed tube with 15% hydrochloric acid and by evaporation of the aqueous solution in vacuo, trichloromethylphosphinic acid was obtained, which after careful drying over P_2O_5 in vacuo, crystallized as needles with a m. p. of 87°. Analyses showed that the acid contained a molecule of combined water, which could be removed neither by careful drying of the substance in vacuo in the cold, nor by long heating. Storage of the acid over P_2O_5 for long periods (more than two months) led to its dehydration, which caused an increase of the melting point of the substance to 145° and an increase of the molecular weight.

The trichloromethylphosphinic acid was dibasic; with a solution of $AgNO_3$ it gave a water-insoluble di-silver salt, which had the capacity of decomposing explosively on slight heating (light touch with a heated rod). In an excess of aniline the acid formed the dianiline salt which, being unstable, gradually lost one aniline molecule on storage or on recrystallization, being converted to the monoaniline salt, which also was readily obtained by reaction of the acid with the equivalent quantity of aniline.

This capacity of trichloromethylphosphinic acid to give the dianiline salt, which was noted also for chlorobromomethylphosphinic acid, is explained by the presence of the polyhalogenated methyl radical in these acids. Chloromethylphosphinic and bromomethylphosphinic acids, as we have already noted, even in an excess of aniline, formed only the monoaniline salts. By the reaction of trichloromethylphosphinic acid with diazomethane the dimethyl ester of trichloromethylphosphinic acid, which was a solid crystalline substance with a m. p. of 37°, was obtained quantitatively.

The above-described properties of the esters of trichloromethylphosphinic acid did not agree accurately with those indicated in G. Kamai's works [3, 4, 5, 6].

According to Kamai, the esters of trichloromethylphosphinic acid which he obtained according to the reaction:

$$CCl_4 + P(OR)_3 \rightarrow CCl_3PO(OR)_2 + RCl,$$

on saponification with hydrochloric acid under conditions similar to those which we used, gave not trichloromethylphosphinic, but phosphorous acid, according to the scheme:

$$CCl_3PO(OR)_2 + 2HCl + H_2O \rightarrow 2RCl + 3HCl + (HO)_2P(O)COOH,\ (HO)_2P(O)COOH \rightarrow CO_2 + P(OH)_3.$$

This circumstance induced us to repeat Kamai's experiment. By careful distillation of the trimethylphosphite and triethylphosphite reaction products with CCl_4, we obtained the methyl and ethyl esters, respectively, which were similar in constants to those which we obtained earlier (see Table).

Saponification of these esters under the conditions which we used (4 hours in an ampoule with 15% HCl at 140-150°) gave trichloromethylphosphinic acid, as did also the saponification of the esters which we obtained earlier.

Thus, Kamai's negative results in his attempts to obtain trichloromethylphosphinic acid can be explained only by the use of an unsuccessful method of separation of the saponification products of the esters. For an additional confirmation of the identity of the esters, obtained by the reactions of $CCl_3PCl_4 + C_2H_5ONO$ and $CCl_4 + P(OC_2H_5)_3$, we

planned to carry out their reaction with aniline which, according to Kamai [5], led to the anilide of the dialkylphosphoric acid.

$$CCl_3PO(OR)_2 + C_6H_5NH_2 \rightarrow CCl_3H + C_6H_5NHPO(OR)_2.$$

In attempts to carry out this reaction with the esters obtained by both the first and second scheme, it was noted that no visible reaction of the esters with aniline took place at room temperature. However, after a 2- or 3-hour boiling of the mixture of the components in toluene and after cooling the reaction mixture, in both cases identical acicular crystals of a substance separated, which according to analyses, proved to be not the anilide, but the anilide acid salt of the ester of trichloromethylphosphinic acid $CCl_3PO(OC_2H_5)OH \cdot C_6H_5NH_2$.

Similarly, under the conditions described, the dimethyl ester of trichloromethylphosphinic acid also reacts with aniline, forming the acid salt of the ester $CCl_3PO(OCH_3)OH \cdot C_6H_5NH_2$.

Thus, the reaction between the compounds indicated consists not of the cleavage of the C–P bond in the molecule of the ester of trichloromethylphosphinic acid, but apparently consists of the alkylation of aniline by it.

$$CCl_3PO(OR)_2 + C_6H_5NH_2 \rightarrow CCl_3PO(OR)OH + C_6H_5NHR$$
$$CCl_3PO(OR)OH + C_6H_5NH_2 \rightarrow CCl_3PO(OR)OH \cdot C_6H_5NH_2.$$

Constant	Esters obtained by the new methods		Isolated by us from the products obtained by Kamai's method		Kamai's data	
	methyl	ethyl	methyl	ethyl	methyl	ethyl
boiling point	Crystals 109° (9 mm)	124° (15 mm)	109° (9 mm)	123° (13 mm)	Liquid 122° (12 mm)	122-123° (12 mm)
melting point	37°	–	36-37°	–	–	–
d_0	(50°) 1.4810	(14°) 1.3700	(50°) 1.4830	(14°) 1.3710	(15°) 1.4594	(14°) 1.3664
n_D	(50°) 1.4615	(20°) 1.4615	(50°) 1.4620	(20°) 1.4620	(14°) 1.4580	(14°) 1.4585

Lugovkin and Arbuzov [7] showed the ease of such an alkylation of aromatic amines by the esters of the acids of pentavalent phosphorus (acid chloride of dialkylphosphoric acid).

In a series of works, Todd and Atherton [8] described the phosphorylation reaction of amines, which proceeded by their reaction with dialkylphosphites in a CCl_4 medium, with the formation of amides of dialkylphosphoric acid.

$$(RO)_2P(O)H + CCl_4 + NHR_2 \rightarrow \left[(RO)_2P(O)CCl_3\right] + NHR_2 \cdot HCl$$

$$\left[(RO)_2P(O)CCl_3\right] + NHR_2\begin{pmatrix}\text{or } NH_3\\ \text{or } NH_2R\end{pmatrix} \rightarrow (RO)_2PONR_2 + CHCl_3.$$

Aniline was also present in a number of investigations of the amines by Todd and Atherton. In not one case did the authors themselves succeed in isolating an intermediate ester of trichloromethylphosphinic acid, arising according to this scheme. Kamai, indicating the property of the esters of trichloromethylphosphinic acid to undergo cleavage by the action of amines (aniline), with the formation of the products described by Todd and Atherton, assumed that his observations confirmed the validity of the above-cited reaction mechanism. At least for aniline, the results of the present investigation, obtained under the conditions described, did not confirm Kamai's data, and placed in doubt the correctness of the scheme of the phosphorylation mechanism of the amines proposed by Todd and Atherton.

EXPERIMENTAL

Chlorination of chloromethyldichlorophosphine. Production of phosphorus trichloromethyltetrachloride. CCl_3PCl_4. Dry chlorine was passed into a solution of 15 g of chloromethyldichlorophosphine in 250 ml of carbon tetrachloride at a temperature of −5-0° until the appearance of the non-fading color of chlorine. Then the temperature in the reaction mixture rose to +30-35°, and the chlorination was continued for 30 minutes more, after which the solvent was removed in vacuo (bath temperature did not exceed 35°). In the residue were colorless, hygroscopic crystals with a m. p. of 125-126° (with decomp.) (in sealed capillary). The yield was quantitative. The substance

hydrolyzed very slowly and non-quantitatively (3 chlorine atoms were hydrolyzed). 0.5 N alkali, with boiling, brought about the complete decomposition of the substance.

3.085 mg sub.: 0.480 mg CO_2. 3.560 mg sub.: 0.525 mg CO_2. 0.085 g sub. (in bomb): 20.16 ml 0.1 N $AgNO_3$. 0.3400 g sub.: 16 g benzene: Δt 0.386°. Found %: C 4.24, 4.02; Cl 84.21; P 10.16. M 281. CCl_3PCl_4. Calculated %: C 4.27; Cl 85.08; P 10.65; M 291.5.

Production of the acid dichloride of trichloromethylphosphinic acid – CCl_3POCl_2. 10 g of chloromethyldichlorophosphine was chlorinated in carbon tetrachloride as described above, until the formation of CCl_3PCl_4. Then the excess of chlorine and most of the solvent were driven off in vacuo at +30°, dry SO_2 was passed into the remaining solution (about 30-40 ml), at first in the cold (ice water), and then for 30 minutes at +30°.

The rest of the solvent was removed in vacuo. A dry, colorless substance remained, which consisted of fine crystals which were hygroscopic and which decomposed on storage in the air. The substance had a m. p. of 155°, dissolved well in CCl_4 and in benzene, but dissolved little in cold water. By the action of 0.5 N potassium hydroxide on the substance at room temperature, hydrolysis proceeded readily with the splitting off of 1 chlorine atom, but the hydrolysis did not go to completion (splitting off of 2 chlorine atoms). The chlorine, bound to both the phosphorus and the carbon, was hydrolyzed on heating.

5.320 mg sub.: 1.045 mg CO_2. 5.310 mg sub.: 0.985 mg CO_2. 0.0641 g sub. (in bomb): 13.43 ml 0.1 N $AgNO_3$. 0.110 g sub.: 0.8946 g molybdate. 0.1012 g sub.: 0.8351 g molybdate. 0.4690 g sub.: 16 g benzene: Δt 0.600°. Found %: C 5.35, 5.06; Cl 74.29; P 13.48, 13.64. M 246. CCl_3POCl_2. Calculated %: C 5.08; Cl 75.06; P 13.16; M 236.5.

Production of the monoanilide – $CCl_3PO(Cl)NHC_6H_5$. 3.7 g of aniline was added to 2.3 g of CCl_3POCl_2 in 15 ml of benzene. After 3 hours the acid chloride of aniline was filtered by suction; the rest of the aniline was removed by washing with acidified water. The solvent was removed after drying the benzene solution over sodium sulfate. The oil which remained quickly crystallized (1.5 g). After recrystallization from aqueous alcohol and then from a mixture of hexane with carbon tetrachloride, it consisted of thin prisms with a m. p. of 113-113.5°.

10.42 mg sub.: 7.172 ml 0.02 N $AgNO_3$. 10.20 mg sub.: 7.023 ml 0.02 N $AgNO_3$. 3.910 mg sub.: 0.1695 ml N_2 (22°, 751 mm); 4.893 mg sub.: 0.1998 ml N_2 (22°, 751 mm). 0.1055 g sub.: 16 g benzene: Δt 0.120°. Found %: Cl 48.82, 48.65; N 4.93, 4.55. M 286. $CCl_3PO(Cl)NHC_6H_5$. Calculated %: Cl 48.47; N 4.77, M 293.

Production of the dianilide of trichloromethylphosphinic acid $CCl_3PO(NHC_6H_5)_2$. An excess of aniline (15 g) was added to 5 g of the acid chloride of trichloromethylphosphinic acid, dissolved in 30 ml of benzene, and the mixture was left for three days. Then the reaction mixture was washed with acidified water in order to remove the acid chloride of aniline and the excess of aniline; a benzene solution was collected and dried over sodium sulfate. The almost pure dianilide (2.2 g) came down as fine, white acicular crystals after removal of a portion of the benzene. The remaining solvent was evaporated in vacuo at 40°; the residue was an oil which crystallized after a day (4.5 g). After repeated recrystallization from water it consisted of colorless needles with a m. p. of 172°.

9.495 mg sub.: 4.025 ml 0.02 N $AgNO_3$. 9.615 mg sub.: 4.097 ml 0.02 N $AgNO_3$. 5.337 mg sub.: 0.4070 ml N_2 (21°, 745 mm). 5.285 mg sub.: 0.4000 ml N_2 (21°, 745 mm). 0.2010 g sub.: 16 g benzene: Δt 0.192°. Found %: Cl 30.06, 30.22; N 8.41, 8.43. M 331.5. $CCl_3PO(NHC_6H_5)_2$. Calculated %: Cl 30.47; N 8.02. M 349.5.

Production of the diethyl ester of trichloromethylphosphinic acid $CCl_3PO(OC_2H_5)_2$. 30 ml of ethyl nitrite (2.5-3 fold excess) was condensed in 10 g of CCl_3PCl_4, cooled to –50°, then the cooling was stopped and the mixture was boiled under reflux for 4 hours, with a condenser with brine cooling, the temperature of which rose gradually from –5° to +10°; moreover, the solution grew lighter, depending on the degree of removal of nitrosyl chloride. The reaction was completed when drops of the solution of the aqueous hydrolyzate ceased to precipitate silver from a solution of $AgNO_3$, after which the mixture was repeatedly distilled. 4.5 g of a fraction with a b. p. of 104-105.5° (6 mm), or 124° (15 mm), was collected. It was a colorless, oily liquid with a pleasant fruity odor:

d_0^{14} 1.3700, n_D^{20} 1.4615.

3.780 mg sub.: 3.240 mg CO_2; 1.190 mg H_2O. 5.190 mg sub.: 4.385 mg CO_2; 1.730 mg H_2O. 0.0976 g sub.:* 11.65 ml 0.1 N $AgNO_3$. 0.2020 g sub.: 16 g benzene: Δt 0.260°. Found %: C 23.37, 23.04; H 3.52, 3.72; Cl 42.37. M 248.5. $CCl_3PO(OC_2H_5)_2$. Calculated %: C 23.50; H 3.90; Cl 41.63. M 255.5.

* A weighed portion was sealed in a tube with 5 ml of C_2H_5OH containing 1 g of dissolved Na, and heated for 2 hours at 150°. Then the contents were boiled in a flask in order to remove the gases, and acidified with HNO_3 and titrated with $AgNO_3$.

Production of trichloromethylphosphinic acid – $CCl_3PO(OH)_2$. 4.5 g of $CCl_3PO(OC_2H_5)_2$, obtained as described above, was heated in an ampoule for 4 hours at 140° with a 5-fold quantity by volume (15 ml) of 15% hydrochloric acid. On cooling, the reaction mixture separated into two layers. The upper layer (about 2 g) consisted of ethyl chloride. The lower layer was evaporated in vacuo on the water bath at 70-80°. The residue crystallized. After a 2-day drying of the crystals in a vacuum-desiccator over P_2O_5, they were recrystallized from benzene (solubility 2 g per 200 ml of boiling benzene) or from carbon tetrachloride (solubility 1 g per 200 ml of boilin CCl_4). The fine needles with a m. p. of 87° were readily soluble in acetone, ether and water.

6.300 mg sub.: 1.300 mg CO_2; 1.280 mg H_2O. 5.390 mg sub.: 1.125 mg CO_2; 1.105 mg H_2O. 14.460 mg sub.: 10.21 ml 0.02 N $AgNO_3$. 11.890 mg sub.: 8.36 ml 0.02 N $AgNO_3$. 0.0256 g sub.: 0.2248 g molybdate. 0.0312 g sub.: 0.2715 g molybdate. 2.215 mg sub.: 1.108 ml CH_4 (0°, 760 mm). 2.710 mg sub.: 1.055 ml CH_4. 0.1524 g sub.: 7.65 ml 0.1 N KOH (by methyl orange) 13.75 ml (by phenolphthalein) 0.1786 g sub.: 9.10 ml 0.1 N KOH (by methyl orange) 16.13 ml (by phenolphthalein) Found %: C 5.63, 5.67; H 2.26, 2.34; Cl 49.88, 50.06; P 14.50, 14.39; active H 1.755, 1.728. Equiv 197, 194 (by methyl orange) 109, 108.5 (by phenolphthalein) $CCl_3PO(OH)_2 \cdot H_2O$. Calculated %: C 5.52; H 1.83; Cl 49.08; P 14.28; active H 1.83, Equiv. 217.5, 108.6.

Thus, the crystals with a m. p. of 87° were the monohydrate of trichloromethylphosphinic acid. Heating of the substance for 2 hours at 100° led to no loss of the water of crystallization. The acid dehydrated on standing over P_2O_5 in a vacuum-desiccator for 2-3 months, which led to an increase of the melting point of the sample to 145°, to the loss of active hydrogen, and to an increase of the molecular weight (340 in acetophenone).

Production of the silver salt of trichloromethylphosphinic acid – $CCl_3PO(OAg)_2$. An excess of a concentrated solution of $AgNO_3$ was added to 0.5 g of trichloromethylphosphinic acid (m. p. 87°) dissolved in 5 ml of water. A finely-crystalline precipitate which was difficultly soluble in water, but soluble in dilute HNO_3, came down immediately. The precipitate was filtered off, washed with alcohol and ether, and dried. In the dry form the substance exploded on touching a slightly heated rod to it. The yield was quantitative.

0.1117 g sub.: 5.30 ml 0.1 N NH_4CNS. 0.0775 g sub.: 3.75 ml 0.1 N NH_4CNS. Found %: Ag 51.19, 52.19. $CCl_3PO(OAg)_2$. Calculated %: Ag 52.21.

Production of the dianiline salt of trichloromethylphosphinic acid $CCl_3PO(OH)_2 \cdot 2C_6H_5NH_2$. An excess of aniline (1 g) was added to a suspension of 0.5 g of the trichloromethylphosphinic acid with a m. p. of 87° in 15 ml of benzene. After two days the insoluble dianiline salt was filtered off and recrystallized from alcohol containing 2% aniline. The fine needles were kept in a desiccator over aniline. The substance did not melt up to 220°, but decomposed. The yield was quantitative.

3.275 mg sub.: 0.2280 ml N_2 (28°, 740 mm). 3.010 mg sub.: 0.2120 ml N_2 (28°, 740 mm). 10.100 mg sub.: 3.950 ml 0.02 N $AgNO_3$. 11.300 mg sub.: 4.400 ml 0.02 N $AgNO_3$. Found %: N 7.80, 7.70; Cl 27.77, 27.65. $CCl_3PO(OH_2) \cdot 2C_6H_5NH_2$. Calculated %: N 7.27; Cl 27.66.

Production of the monoaniline salt of trichloromethylphosphinic acid – $CCl_3PO(OH)_2 \cdot C_3H_5NH_2$. A mixture of 50 ml of benzene, 2 g of trichloromethylphosphinic acid and 0.93 g of aniline was left for two days. Then the precipitate (2.9 g) was separated and recrystallized from acetic acid or from water. It consisted of flaky crystals which did not melt up to 220°.

4.140 mg sub.: 0.1860 ml N_2 (22°, 744 mm). 5.105 mg sub.: 0.2350 ml N_2 (22°, 744 mm). Found %: N 5.22, 5.09. $CCl_3PO(OH)_2 \cdot C_6H_5NH_2$. Calculated %: N 4.78.

Production of the dimethyl ester of trichloromethylphosphinic acid –$CCl_3PO(OCH_3)_2$. A solution of 3.2 g (3 moles) of diazomethane in 150 ml of ether was added to a solution of 5 g (1 M) of trichloromethylphosphinic acid in 50 ml of ether at a temperature of –10°. After removal of the ether about 5 g of a residue was obtained, which distilled almost completely at 110-113° (9 mm). Pure dimethyl ester with a b. p. of 109° (9 mm) and a m. p. +37° was obtained by repeated distillation.

d_0^{50} 1.4810, n_D^{50} 1.4615.

0.1024 mg sub.: 13.35 ml 0.1 N $AgNO_3$. 0.0886 g sub.: 46.10 ml 0.1N $Na_2S_2O_3$. 0.0707 g sub.: 36.77 ml 0.1 N $Na_2S_2O_3$. 0.4810 g sub.: 16 g benzene: Δt 0.665°. Found %: Cl 46.23; OCH_3 26.90, 28.89. M 232. $CCl_3PO(OCH_3)_2$. Calculated %: Cl 46.81; OCH_3 27.10. M 227.5.

Production of the dimethyl ester of trichloromethylphosphinic acid by Kamai's method. The reaction was carried out exactly according to the description [3]. A fraction with a b. p. of 109° (9 mm) and a m. p. of 37° was separated by a precise distillation. The constants of the substance – d_0^{50} 1.4830 and n_D^{50} 1.4620 – agreed exactly with those obtained for the ester formed by the reaction of trichloromethylphosphinic acid with diazomethane.

Production of the diethyl ester of trichloromethylphosphinic acid by Kamai's method. The reaction was carried out exactly according to the description [3]. After a precise distillation a substance with a b. p. of 122-123° (13 mm), d_0^{14} 1.3710, n_D^{20} 1.4620 was separated, i. e., a substance with constants which agreed with those of the diethyl ester which we obtained earlier and which differed somewhat from that described by Kamai [b. p. 122-123° (12 mm), d_0^{14} 1.3664, n_D^{14} 1.4585].

Saponification of the diethyl ester of trichloromethylphosphinic acid obtained by Kamai's method. 4.5 g of the diethyl ester of trichloromethylphosphinic acid, obtained by Kamai's method, was saponified with 15 ml of 15% hydrochloric acid under conditions which we employed for the production of trichloromethylphosphinic acid. After removal of the aqueous solution in vacuo, 4.1 g of a crystalline substance remained, which after drying and recrystallization from benzene had a m. p. of 87°, and proved to be identical with the trichloromethylphosphinic acid obtained as described earlier (sample of a mixture of the indicated acids gave no depression on melting).

Reaction of the diethyl ester of trichloromethylphosphinic acid with aniline. 1 g of the diethyl ester of trichloromethylphosphinic acid (obtained by any of the methods described above) was mixed with 3 ml of aniline and 30 ml of toluene and boiled for 2 hours. Crystals precipitated from the reaction mixture, on cooling. On the next day they were filtered off (1.2 g) and washed with benzene. The reaction took place identically esters. Fine needles with a m. p. of 174-176° (with decomp.) were obtained.

5.170 mg sub.: 6.270 mg CO_2; 2.050 mg H_2O. 16.910 mg sub.: 3.116 ml 0.05 N $AgNO_3$. 4.599 mg sub.: 0.2060 ml N_2 (23°, 735 mm). 4.490 mg sub.: 0.1990 ml N_2 (23°, 735 mm). 0.0588 g sub.: 10.71 ml 0.1 N $Na_2S_2O_3$. 0.0722 g sub.: 13.15 ml 0.1 N $Na_2S_2O_3$. 0.1015 g sub.: 3.20 ml 0.1 N KOH (by phenolphthalein) 0.1490 g sub.: 4.73 ml 0.1 N KOH (by phenolphthalein) Found %: C 33.08; H 4.43; Cl 32.67; N 4.99, 4.36; OC_2H_5 13.67, 14.04 Equiv. 317, 320.5. $CCl_3PO(OC_2H_5)OH \cdot C_6H_5NH_2$. Calculated %: C 33.67; H 4.05; Cl 33.23; N 4.93; OC_2H_5 13.67 Equiv. 314.0.

Reaction of the dimethyl ester of trichloromethylphosphinic acid with aniline. 1 g of the dimethyl ester of trichloromethylphosphinic acid (obtained by any of the methods described above) was mixed with 3 ml of aniline and 30 ml of toluene and boiled for 2 hours. On cooling, crystals – colorless needles – separated from the reaction mixture. On the next day they were separated (1 g) and washed with benzene. The product obtained was similar to that described above and had a m. p. of 172° (with decomp.)

3.813 mg sub.: 4.355 mg CO_2; 1.091 mg H_2O. 11.050 mg sub.: 5.340 ml 0.02 N $AgNO_3$. 4.720 mg sub.: 0.1890 ml N_2 (25°, 761 mm). 4.775 mg sub.: 0.2030 ml N_2 (25°, 761 mm). 0.0630 g sub.: 12.0 ml 0.1 N $Na_2S_2O_3$. 0.0396 g sub.: 7.45 ml 0.1 N $Na_2S_2O_3$. 0.1374 g sub.: 4.60 ml 0.1 N KOH (by phenolphthalein). 0.0949 g sub.: 3.16 ml 0.1 N KOH (by phenolphthalein). Found %: C 31.15; H 3.20; Cl 34.31; N 4.65, 4.89; OCH_3 9.85, 9.74. Equiv. 300, 300. $CCl_3PO(OCH_3)OH \cdot C_6H_5NH_2$. Calculated %: C 31.32; H 3.25; Cl 34.75; N 4.56; OCH_3 10.13. Equiv. 306.5.

Production of phosphorus dichloromethyltetrachloride. The calculated quantity of a solution of chlorine in CCl_4 was slowly introduced dropwise into 5 g of chloromethyldichlorophosphine dissolved in 150 mg of carbon tetrachloride, with cooling (ice and salt). The chlorine color in the reaction mixture disappeared rapidly. On addition of the total quantity of chlorine, most of the solvent was removed in vacuo, and a finely-crystalline, white, hygroscopic phosphorus dichloromethyltetrachloride precipitate, which deliquesced in the air, came down.

0.1770 g sub.: (in 25 ml 0.5 N KOH): 27.30 ml 0.1 N $AgNO_3$. 0.1520 g sub.: (in 25 ml 0.5 N KOH): 23.50 ml 0.1 N $AgNO_3$. Found %: Cl hyd. 54.76, 54.89. CCl_2HPCl_4. Calculated %: Cl hyd. 55.25.

Production of dichloromethylphosphinic acid – $CCl_2HPO(OH)_2$. 1 g of CCl_2HPCl_4 was hydrolyzed by 3 ml of warm (40°) water. After removal of the excess water in vacuo, and after drying the substance over P_2O_5 in a desiccator, it consisted of course, acicular crystals, which rapidly moistened in the air, and had a m. p. of 53°. Its m. p. was 115° after repeated recrystallization from benzene.

5.065 mg sub.: 1.272 mg CO_2; 0.585 mg H_2O. 4.090 mg sub.: 1.056 mg CO_2; 0.477 mg H_2O. 10.285 mg sub.: 6.295 ml 0.02 N $AgNO_3$. 5.115 mg sub.: 3.082 ml 0.02 N $AgNO_3$. Found %: C 6.85, 5.98; H 1.29, 1.30; Cl 43.43, 42.68. $CCl_2HPO(OH)_2$. Calculated %: C 7.27; H 1.80; Cl 43.03.

Bromination of chloromethyldichlorophosphine. Production of chlorobromomethylphosphinic acid – $ClBrCHPO(OH)_2$. An excess of bromine (10 g) in 25 ml of CCl_4 was introduced dropwise, with stirring, into a cooled (ice and salt) solution of 5 g of $ClCH_2PCl_2$ in 26 ml of CCl_4. Then the bath temperature rose to 50° and was maintained so for 2 hours, after which the solvent was removed in vacuo, and the residue was decomposed with water. The substance crystallized on standing over P_2O_5 and KOH in a vacuum-desiccator.

The crystalline substance (3.5 g) was pressed on a dry porous plate. The product was extremely hygroscopic and immediately deliquesced in the air. The aniline salt was obtained by pouring together a benzene solution of the acid with an excess of aniline. After its recrystallization from alcohol, the fine needles with a m. p. of 180-185° (with decomp.) contained chlorine and bromine.

4.805 mg sub.: 0.2860 ml N_2 (30°, 746 mm). 3.770 mg sub.: 0.2270 ml N_2 (30°, 746 mm). Found %: N 6.59, 6.69; $ClBrCHPO(OH)_2 \cdot 2C_6H_5NH_2$. Calculated %: N 7.08.

SUMMARY

1. The action of chlorine and bromine on chloromethyldichlorophosphine was investigated, and it was found that di- and trihalomethylphosphinic derivatives formed in this way. Dichloromethyl-, chlorobromomethyl-, and trichloromethylphosphinic acids were isolated and characterized (salts, ester, and acid halides).

2. The literature data notwithstanding, it was found that the esters of trichloromethylphosphinic acid can be: a) normally converted to trichloromethylphosphinic acid by saponification, and b) by reaction with aniline converted to the corresponding acid esters in this reaction no cleavage of the C–P bond was observed.

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Received February 12, 1954.

• T. p. = C. B. Translation pagination.